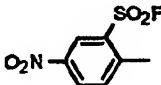




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/GB94/02831 <b>(22) International Filing Date:</b> 30 December 1994 (30.12.94)  <b>(30) Priority Data:</b> 9400972.7      19 January 1994 (19.01.94)      GB  <b>(71) Applicant (for all designated States except US):</b> ZENECA LIMITED [GB/GB]; 15 Stanhope Gate, London W1Y 6LN (GB).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> HALL, Nigel [GB/GB]; 35 Newton Drive, Greenmount, Bury BL8 4DH (GB).  <b>(74) Agents:</b> GILES, David, Eric et al.; Intellectual Property Group, Zeneca Specialties, P.O. Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB).		<b>(81) Designated States:</b> AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> MONOAZO DYES CONTAINING A FLUOROSULPHONYL GROUP AND USE THEREOF  <b>(57) Abstract</b>  <p>A process for colouring a synthetic textile material or fibre blend thereof which comprises applying to the synthetic textile material a compound or mixture thereof, which is free from water solubilising groups, of the Formula (1) A-N=N-D, wherein: A and D each independently is an optionally substituted heterocyclic or carbocyclic group and at least one of A or D carries directly at least one -SO<sub>2</sub>F group or carries a substituent to which at least one -SO<sub>2</sub>F group is attached except for 4-(4-fluorosulphonylphenylazo)-N,N-dimethylaniline, provided that one of A or D is not 3,5-difluorosulphonylthien-2-yl, optionally substituted 1-phenyl-pyrazol-4-yl-5-one or (a) or that one of A or D does not carry an -NCH<sub>2</sub>CH(OH)CH<sub>2</sub>Cl, -NCOCH<sub>2</sub>Cl or -NCH<sub>2</sub>CH<sub>2</sub>SO<sub>2</sub>F substituent. The presence of one or more -SO<sub>2</sub>F groups in a dye molecule generally improves the properties of that dye and confers surprisingly good wet fastness and light fastness properties.</p> <div style="text-align: right; margin-top: 20px;">  <span style="margin-left: 20px;">(a)</span> </div>		

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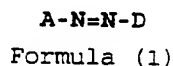
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# MONOAZO DYES CONTAINING A FLUOROSULPHONYL GROUP AND USE THEREOF

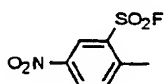
The present invention relates to a process for colouring synthetic textile materials, to synthetic textiles when coloured, to a process for the mass coloration of plastics, to plastics when coloured, to certain novel azo dyes and to compositions containing azo dyes.

According to the present invention there is provided a process for colouring a synthetic textile material or fibre blend thereof which comprises applying to the synthetic textile material a compound or mixture thereof, which is free from water solubilising groups, of Formula (1):



wherein:

A and D each independently is an optionally substituted heterocyclic or carbocyclic group and at least one of A or D carries directly at least one  $-\text{SO}_2\text{F}$  group or carries a substituent to which at least one  $-\text{SO}_2\text{F}$  group is attached except for 4-(4-fluorosulphonylphenylazo)-N,N-dimethylaniline, provided that one of A or D is not 3,5-difluorosulphonylthien-2-yl, optionally substituted 1-phenyl-pyrazol-4-yl-5-one or



or that one of A or D does not carry an  $-\text{NCH}_2\text{CH}(\text{OH})\text{CH}_2\text{Cl}$ ,  $-\text{NCOCH}_2\text{Cl}$  or  $-\text{NCH}_2\text{CH}_2\text{SO}_2\text{F}$  substituent.

Different compounds of Formula (1) may be mixed or the compounds of Formula (1) may be mixed with dyes which do not contain an  $-\text{SO}_2\text{F}$  group. The mixtures may be simple physical mixtures or may be mixed crystals formed for example by co-crystallisation. Such mixtures generally show improvement in dyeing properties. Crystalline modifications of compounds of Formula (1) exist and it is intended that the present definition includes such crystalline modifications which may be formed by heat treatment.

The presence of one or more  $-\text{SO}_2\text{F}$  groups in a dye molecule generally improves the properties of that dye and confers surprisingly good wet-fastness and light-fastness properties.

According to a first embodiment of the present invention

there is provided a process for colouring a synthetic textile material or fibre blend thereof which comprises applying to the synthetic textile material a compound or mixture thereof, which is free from water solubilising groups, of Formula (1) wherein A and D each independently is an optionally substituted heterocyclic or carbocyclic group in which at least one of A or D carries directly at least one  $-\text{SO}_2\text{F}$  group or carries a substituent to which at least one  $-\text{SO}_2\text{F}$  group is attached and at least one of A or D carries directly at least one ester group or carries a substituent to which at least one ester group is attached.

Azo dyes containing both an  $-\text{SO}_2\text{F}$  and an ester group have improved performances in wash fastness properties over azo dyes carrying only an  $-\text{SO}_2\text{F}$  group.

The synthetic textile material may be selected from secondary cellulose acetate, cellulose triacetate, polyamide, polyacrylonitrile and aromatic polyester. The synthetic textile material is preferably polyamide or aromatic polyester, more preferably aromatic polyester such as polyhexamethylene adipamide or polyethylene terephthalate and especially polyethylene terephthalate. Fibre blends may comprise mixtures of different synthetic textile materials or mixtures of synthetic and natural textile materials. Preferred fibre blends are those of polyester cellulose such as polyester-cotton. The textile materials or blends thereof may be in the form of filaments, loose fibres, yarn, woven or knitted fibres.

According to a second embodiment of the present invention there is provided a process for colouring a polyester textile material or fibre blend thereof which comprises applying to the polyester textile material a compound or mixture thereof, which is free from water solubilising groups, of Formula (1) in which A and D are as herein before defined except for 4-(4-fluorosulphonylphenylazo)-N,N-dimethylaniline, provided that one of A or D is not 3,5-difluorosulphonylthien-2-yl, optionally substituted 1-phenylpyrazol-4-yl-5-one or 4-nitro-2-fluorosulphonylphenyl or that one of A or D does not carry an  $-\text{NCH}_2\text{CH}_2\text{SO}_2\text{F}$  substituent.

The dyes of Formula (1) preferably have low solubility in water, typically less than 1% preferably less than 0.5% and especially less than 0.2% solubility in water. The dyes of Formula (1) are thus free from water solubilising groups such as  $-\text{SO}_3\text{H}$ ,  $-\text{CO}_2\text{H}$ ,  $-\text{PO}_3\text{H}$  and quaternary amino.

The compounds of Formula (1), optionally in conjunction with other disperse dyes may be applied to the synthetic textile materials or fibre blends thereof by methods which are conventionally employed in dyeing disperse dyes to such materials and fibre blends.

The process conditions may be selected from the following:

- 1) exhaust dyeing at a pH of from 4 to 6.5, at a temperature of from

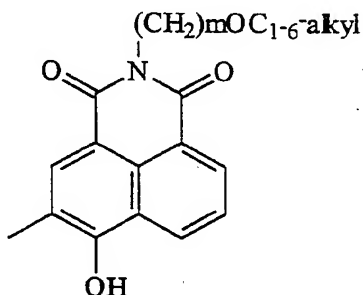
- 125°C to 140°C for from 10 to 120 minutes and under a pressure of from 1 to 2 bar, a sequestrant may be optionally be added;
- ii) continuous dyeing at a pH of from 4 to 6.5, at a temperature of from 190°C to 225°C for from 15 seconds to 5 minutes, a migration inhibitor may optionally be added;
- iii) printing direct at a pH of from 4 to 6.5, at a temperature of from 160°C to 185°C for 4 to 15 minutes for high temperature steaming, or at a temperature of from 190°C to 225°C for 15 seconds to 5 minutes for bake fixation with dry heat or at a temperature of from 120°C to 140°C and 1 to 2 bar for 10 to 45 minutes for pressure steaming, wetting agents and thickeners (such as alginates) of from 5 to 100% by weight of the dye may be optionally be added;
- iv) discharge printing (by padding the dye onto the textile material, drying and overprinting) at a pH of from 4 to 6.5, migration inhibitors and thickeners may optionally be added;
- v) carrier dyeing at a pH of from 4 to 6.5, at a temperature of from 95°C to 100°C using a carrier such as methylnaphthalene, diphenylamine or 2-phenylphenol, sequesterants may optionally be added; and
- vi) atmospheric dyeing of acetate, triacetate and nylon at a pH of from 4 to 6.5, at a temperature of 85°C for acetate or at a temperature of 90°C for triacetate and nylon for from 15 to 90 minutes, sequesterants may optionally be added.

In all the above processes the compound of Formula (1) is applied as a dispersion comprising from 0.001% to 4% of the compound in aqueous medium.

The present compounds generally provide coloured textile material which shows good fastness to washing, light and heat.

The heterocyclic group represented by A and D may be selected from thienyl, thiazolyl, isothiazolyl, pyrazolyl, imidazolyl, pyridyl, pyridonyl, 1,2,4- and 1,3,4-thiadiazolyl, furanyl, pyrrolyl, pyridazyl, pyrimidyl, pyrazinyl, benzothiazolyl, benzoisothiazolyl, quinolinyl, isoquinolinyl, indolyl, pyridothiazolyl, pyridoisothiazolyl, 1,2,3-triazolyl and 1,2,4-triazolyl. The carbocyclic group represented by A or D may be phenyl or naphthyl.

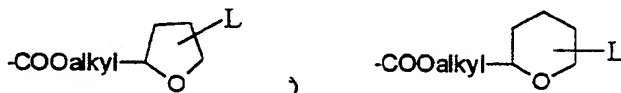
For the avoidance of doubt optionally substituted isoquinolinyl represented by A includes structures of the formula:



in which m is from 1 to 4 and m is preferably 3.

A and D each independently is preferably thienyl, phenyl, naphthyl, thiazolyl, isothiazolyl, pyridonyl, quinolinyl more preferably thien-2-yl, phenyl, naphth-1-yl, naphth-2-yl, thiazol-2-yl, isothiazol-5-yl, pyrid-4-one-5-yl or quinolinyl. A is especially preferably thien-2-yl or phenyl and D is especially preferably phenyl or naphth-1-yl.

Examples of suitable substituents for A and D are cyano, hydroxy, nitro, fluoro, chloro, bromo, iodo, fluorosulphonyl, trifluoromethyl, alkyl, alkoxy, aryl, aryloxy, fluorosulphonylaryl, fluorosulphonylaryloxy, -COalkyl, -COOalkyl, -OCOalkyl, -COaryl, -COOaryl, -OCOaryl, -NHCOalkyl, -NHCOaryl, -NHSO<sub>2</sub>alkyl, -NHSO<sub>2</sub>aryl, -Salkyl, -Saryl, -SO<sub>2</sub>alkyl, -SO<sub>2</sub>aryl, -SCN or -NR<sup>1</sup>R<sup>2</sup> in which R<sup>1</sup> and R<sup>2</sup> each independently is -H, alkyl, aryl or cycloalkyl all the alkyl, alkoxy, aryl, aryloxy parts of the above substituents for A, D, R<sup>1</sup> and R<sup>2</sup> may optionally be substituted by -OH, -CN, -F, -Cl, -Br, -I, -SO<sub>2</sub>F, alkoxy, alkenyl, phenyl, phenylSO<sub>2</sub>F, aryloxy, aryloxySO<sub>2</sub>F, -N(alkyl)<sub>2</sub>, -OCOalkyl, -OCOalkylCl, -COOalkyl, -COOalkylOH, -COOalkylCN, -COOalkylCOalkyl, -COOalkylphenyl, -OCO phenyl, -CophenylSO<sub>2</sub>F, -OCophenylNO<sub>2</sub>, -OCophenylalkyl, -OCophenylalkoxy, -COOphenyl, -OCO(fluorosulphonylphenyl), -OalkylCN, -COOalkylOalkyl, -COOalkylOphenyl, -OCOalkylOphenyl, -COOalkylOalkylOalkyl, -OCOalkylCOOalkyl, -OalkylCOOalkyl, -OalkylCOOalkylOalkyl, -OalkylCOOalkylCOOalkyl, -OalkylOCOalkylOalkyl, -COOalkylOCOalkyl or -COOalkylCOOalkyl,



in which L is -H or alkyl.

In all of the suitable substituents for A and D each alkyl is preferably C<sub>1-10</sub>-alkyl, each alkoxy is preferably C<sub>1-10</sub>-alkoxy, each alkenyl is preferably C<sub>2-8</sub>-alkenyl each of which may be straight or branched chain, each aryl is preferably phenyl or naphthyl and each heterocyclic group may be any of the groups described above for A and D and each alkyl, alkoxy, alkenyl, aryl, heterocyclic or phenyl group may carry an -SO<sub>2</sub>F substituent. R<sup>1</sup> and R<sup>2</sup> together with the -N atom to which they are attached may form a 5- or 6- membered ring such as morpolino or piperidino.

A further suitable substituent for A and D is a group of Formula R<sup>19</sup>-N-Y-X-W in which

Y is a direct link or C = O,

X is a direct link, optionally substituted alkyl, alkenyl, aryl, heterocyclic, alkylOalkyl, alkylNHalkyl or -NR<sup>20</sup>-Z-

or -O-Z- in which Z is optionally substituted alkyl, alkenyl, aryl, heterocyclic, alkylOalkyl, -alkylNHalkyl or a direct link and R<sup>20</sup> is -H, optionally substituted alkyl, aryl or alkylaryl,

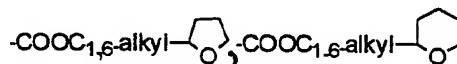
W is -CO<sub>2</sub>R<sup>21</sup>, -OCOR<sup>21</sup>, -OH or -CN in which R<sup>21</sup> is optionally substituted alkyl, aryl, alkylaryl, alkylOalkyl or alkylOH,

R<sup>19</sup> is -H or optionally substituted alkyl.

Where X, Z, R<sup>19</sup>, R<sup>20</sup> or R<sup>21</sup> is or contains alkyl it is preferably C<sub>1-6</sub>-alkyl more preferably C<sub>1-6</sub>-alkyl each of which may be straight or branched chain or cyclic alkyl. Where X or Z is alkenyl it is preferably C<sub>2-6</sub>-alkenyl which may be straight or branched chain or cyclic alkenyl. Where X, Z, R<sup>20</sup> or R<sup>21</sup> is aryl it is preferably phenyl or naphthyl more preferably phenyl. Where X or Z is heterocyclic it may be selected from any of the heterocyclic groups defined above for A. Where X, Z or R<sup>21</sup> is alkylOalkyl it is preferably C<sub>1-6</sub>-alkylOC<sub>1-6</sub>-alkyl each alkyl may be straight or branched chain and the alkylOalkyl group may be cyclic ether. Where X or Z is alkylNHalkyl it is preferably C<sub>1-6</sub>-alkylNHC<sub>1-6</sub>-alkyl in which each alkyl may be straight or branched chain and the alkylNHalkyl group may be a cyclic amine. Where R<sup>20</sup> or R<sup>21</sup> is alkylaryl it is preferably C<sub>1-6</sub>-alkylaryl more preferably C<sub>1-6</sub>-alkylphenyl and especially benzyl or ethylphenyl. Where R<sup>21</sup> is alkylOH it is preferably C<sub>1-6</sub>-alkylOH.

The optional substituents for any of the groups represented by X, Z, R<sup>19</sup>, R<sup>20</sup> or R<sup>21</sup> may be selected from any of the optional substituents listed for A, D, R<sup>1</sup> or R<sup>2</sup>.

Preferred substituents for A and D are cyano, nitro, chloro, bromo, fluorosulphonyl, C<sub>1-6</sub>-alkyl, C<sub>1-6</sub>-alkoxy, -COC<sub>1-6</sub>-alkyl, -NHCOC<sub>1-6</sub>-alkyl, -OCOC<sub>1-6</sub>-alkyl, -COOC<sub>1-6</sub>-alkyl, phenoxy, 4-SO<sub>2</sub>Fphenoxy, R<sup>19</sup>N-Y-X-W in which R<sup>19</sup>, Y, X and W are as herein before defined, and -NR<sup>1</sup>R<sup>2</sup> in which R<sup>1</sup> and R<sup>2</sup> each independently is -H, C<sub>1-6</sub>-alkyl, C<sub>1-6</sub>-alkyl substituted by -OH, -CN, -Cl, phenyl, -OCOC<sub>1-6</sub>-alkyl, -COOC<sub>1-6</sub>-alkyl,



-C<sub>1-4</sub>-alkyl(4-fluorosulphonylphenyl), -OCO(3-fluorosulphonylphenyl), -OCO(4-fluorosulphonylphenyl), -C<sub>2-4</sub>-alkenyl, -COOC<sub>1-6</sub>-alkylOC<sub>1-6</sub>-alkyl, -OC<sub>1-6</sub>-alkylCN, -OC<sub>1-6</sub>-alkylOCOC<sub>1-6</sub>-alkylOC<sub>1-6</sub>-alkyl, -COOalkylOCOalkyl and -COOalkylCOOalkyl or where R<sup>1</sup> and R<sup>2</sup> together with the -N atom to which they are attached form a morpholino or piperidino ring.

The compounds of Formula (1) preferably carry a total of from one to three -SO<sub>2</sub>F groups, more preferably one or two -SO<sub>2</sub>F groups and

especially one  $-SO_2F$  groups.

The compounds of Formula (1) more preferably carry one  $-SO_2F$  group and one ester group.

A number of compounds of Formula (1) used in the above coloration process are novel and according to a further feature of the present invention there is provided a compound of Formula (2):

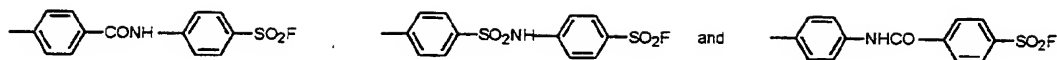


Formula (2)

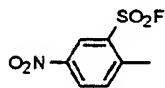
in which:

$A^1$  and  $D^1$  each independently is an optionally substituted heterocyclic or carbocyclic group and at least one of  $A^1$  or  $D^1$  carries directly at least one  $-SO_2F$  group or carries a substituent to which at least one  $-SO_2F$  group is attached except for 4-(4-fluorosulphonylphenylazo)-N,N-dimethylaniline, 4-(4-fluorosulphonylphenylazo)-N,N-diethylaniline, 4-(4-fluorosulphonylphenylazo)-N-ethyl-N-acetoxyethylaniline, 1-(5-fluorosulphonyl-2-methylphenylazo)-2-hydroxynaphthalene, 4-(4-fluorosulphonylphenylazo)-3-(trifluoromethylcarbonylamino)-N-ethyl-N-(2-methoxyethyl)aniline, 4-(4-fluorosulphonylphenylazo)-3-(trifluoromethylcarbonylamino)-N-ethyl-N-(2-cyanoethyl)aniline, 4-(4-fluorosulphonylphenylazo)-2,5-dimethyl-N-ethyl-N-(2-methoxyethyl)aniline, 4-(4-fluorosulphonylphenylazo)-2,5-dimethyl-N-ethyl-N-(2-cyanoethyl)aniline, 4-(4-fluorosulphonylphenylazo)-N-ethyl-N-(2-fluorosulphonylethyl)aniline, 4-(4-fluorosulphonylphenylazo)-N,N-di(2-fluorosulphonylethyl)aniline, 4-(3-fluorosulphonyl-4-methylphenylazo)-3-(trifluoromethylcarbonylamino)-N-ethyl-N-(2-methoxyethyl)aniline, 4-(3-fluorosulphonyl-4-methylphenylazo)-2,5-dimethyl-N-ethyl-N-(2-methoxyethyl)aniline, 4-(3-fluorosulphonyl-4-chlorophenylazo)-3-(trifluoromethylcarbonylamino)-N-ethyl-N-(2-methoxyethyl)aniline, 4-(3-fluorosulphonyl-4-chlorophenylazo)-2,5-dimethyl-N-ethyl-N-(2-methoxyethyl)aniline, 4-(5-fluorosulphonyl-2-methylphenylazo)-1-aminonaphthalene, 4-(5-fluorosulphonyl-2-methylphenylazo)-2-ethoxyaniline, 4-(3-fluorosulphonylphenylazo)-2,5-dimethoxyaniline, 4-(2-chloro-4-nitrophenylazo)-2-methyl-5-fluorosulphonylaniline, provided that  $A^1$  is not 3,5-difluorosulphonylthien-2-yl, optionally substituted pyrazol-4-yl-5-one or N-allylpyrid-2-one-5-yl and provided that  $A^1$  is not





when D<sup>1</sup> carries an -NCH<sub>2</sub>CH(OH)CH<sub>2</sub>Cl substituent and provided that one of A<sup>1</sup> or D<sup>1</sup> is not



and provided that A<sup>1</sup> is not a fluorosulphonylphenyl group when D<sup>1</sup> is an arylamide of an aromatic 2-hydroxycarboxylic acid.

A<sup>1</sup> and D<sup>1</sup> each independently may be any of the heterocyclic groups defined for A above. A<sup>1</sup> and D<sup>1</sup> each independently may be any of the carbocyclic groups defined for A and D above.

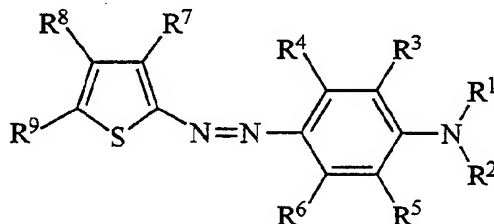
A<sup>1</sup> and D<sup>1</sup> each independently is preferably thienyl, phenyl, naphthyl, thiazolyl, isothiazolyl or pyridonyl, more preferably thienyl, phenyl, thiazolyl, isothiazolyl or pyridonyl and especially thien-2-yl, phenyl, thiazol-2-yl, isothiazol-5-yl or pyrid-4-one-5-yl.

D<sup>1</sup> is preferably phenyl.

Preferred compounds of Formulae (1) and (2) are those in which A or A<sup>1</sup> is phenyl and D or D<sup>1</sup> is phenyl; A or A<sup>1</sup> is thien-2-yl and D or D<sup>1</sup> is phenyl; and A or A<sup>1</sup> is phenyl and D or D<sup>1</sup> is naphth-1-yl.

The optional substituents for A<sup>1</sup> and D<sup>1</sup> are any of those defined for A and D above.

A preferred sub-group of compounds of Formula (1) are those of Formula (3):



Formula (3)

wherein:

R<sup>1</sup> and R<sup>2</sup> each independently is -H or optionally substituted C<sub>1-6</sub>-alkyl or optionally substituted aryl;

R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each independently is -H, -F, -Cl, -Br, -I, -SO<sub>2</sub>F or C<sub>1-6</sub>-alkyl, C<sub>1-6</sub>-alkoxy, C<sub>1-4</sub>alkanoylamino, -NHSO<sub>2</sub>alkyl or Ophenyl each of which may be optionally substituted;

R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup> each independently is -H, C<sub>1-6</sub>-alkyl, -NO<sub>2</sub>, -COOC<sub>1-6</sub>-alkyl, -OCOalkyl,

-Cl, -F, -Br, -I, -COC<sub>1-6</sub>-alkyl, -CN, formyl, protected formyl or -SO<sub>2</sub>F provided that at least one of R<sup>1</sup> to R<sup>9</sup> is -SO<sub>2</sub>F or carries a substituent to which at least one -SO<sub>2</sub>F group is attached and provided that R<sup>7</sup> and R<sup>9</sup> are not both

-SO<sub>2</sub>F.

Where R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup> is or contains alkyl the alkyl may be optionally substituted.

Protected formyl groups include for example oxazolidone, imidazoline, thiazolidine, bisulphite, cyanohydrin, hydrazone and oxime.

The compounds of Formula (3) are novel and accordingly are a further aspect of the present invention.

The optional substituents for groups represented by R<sup>1</sup> to R<sup>9</sup> may be selected from any of the substituents described above for A and D. The optional substituents for R<sup>1</sup> to R<sup>9</sup> are preferably -CN, -OH, -OCOC<sub>1-6</sub>-alkyl, -COOC<sub>1-6</sub>-alkyl, phenyl, -OCophenyl, -OCophenylSO<sub>2</sub>F, phenylSO<sub>2</sub>F, -OphenylSO<sub>2</sub>F, -CO<sub>2</sub>phenylSO<sub>2</sub>F, -COOC<sub>1-6</sub>-alkylOCOC<sub>1-6</sub>-alkyl and -COOC<sub>1-6</sub>-alkylCOOC<sub>1-6</sub>-alkyl.

Preferred compounds of Formula (3) are those in which R<sup>1</sup> and R<sup>2</sup> each independently is -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>, -C<sub>2</sub>H<sub>4</sub>CN, -C<sub>2</sub>H<sub>4</sub>OH, -CH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>, -C<sub>4</sub>H<sub>9</sub>, -CH<sub>2</sub>(4-fluorosulphonylphenyl), -C<sub>2</sub>H<sub>4</sub>(4-fluorosulphonylphenyl), -C<sub>3</sub>H<sub>7</sub>(4-fluorosulphonylphenyl), R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each independently is -H, -Cl, -CH<sub>3</sub>, -OCH<sub>3</sub>, -NHCOCH<sub>3</sub>, -NHCOC<sub>2</sub>H<sub>5</sub>, -NHSO<sub>2</sub>CH<sub>3</sub> or -SO<sub>2</sub>F and R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup> each independently is -H, -NO<sub>2</sub>, -CN, -COCH<sub>3</sub>, -COOC<sub>2</sub>H<sub>5</sub>, -SO<sub>2</sub>F or -CH<sub>3</sub> provided that both R<sup>7</sup> and R<sup>9</sup> are not -SO<sub>2</sub>F.

Especially preferred compounds of Formula (3) are those in which

R<sup>1</sup> and R<sup>2</sup> each independently is -C<sub>2</sub>H<sub>4</sub>CN, -C<sub>2</sub>H<sub>5</sub> or (4-fluorosulphonylphenyl)C<sub>1-6</sub>-alkyl;

R<sup>3</sup> is -H, -OCH<sub>3</sub>, -CH<sub>3</sub> or -SO<sub>2</sub>F;

R<sup>4</sup> and R<sup>5</sup> each independently is -H, -Cl or -SO<sub>2</sub>F;

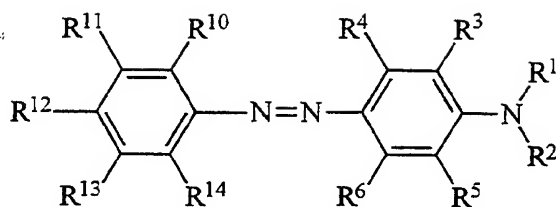
R<sup>6</sup> is -H, -NHCOCH<sub>3</sub>, -NHCOC<sub>2</sub>H<sub>5</sub>, -CH<sub>3</sub> or -SO<sub>2</sub>F;

R<sup>7</sup> is -NO<sub>2</sub>, -COCH<sub>3</sub>, -COOC<sub>2</sub>H<sub>5</sub> or -SO<sub>2</sub>F;

R<sup>8</sup> is -H, -SO<sub>2</sub>F or -Cl;

R<sup>9</sup> is -NO<sub>2</sub>, -SO<sub>2</sub>F or -CHO.

A further preferred sub-group of compounds of Formula (1) are those of Formula (4):



Formula (4)

wherein:

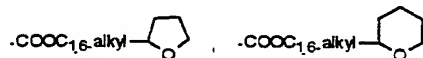
$R^1$  to  $R^6$  are as hereinbefore defined;

$R^{10}$  to  $R^{14}$  each independently is -H, alkoxy, alkyl, -NO<sub>2</sub>, -SO<sub>2</sub>F, -F, -Cl, -Br, -I or -CN;

provided that when  $R^{10}$  is SO<sub>2</sub>F,  $R^{12}$  is not -NO<sub>2</sub> and  $R^{11}$ ,  $R^{13}$  and  $R^{14}$  are not all -H.

Where a group represented by  $R^{10}$  to  $R^{14}$  is alkyl it is preferably C<sub>1-10</sub>-alkyl, more preferably C<sub>1-6</sub>-alkyl. Where a group represented by  $R^{10}$  to  $R^{14}$  is alkoxy it is preferably C<sub>1-10</sub>-alkoxy more preferably C<sub>1-6</sub>-alkoxy.

Compounds of Formula (4) are preferably those in which  $R^1$  and  $R^2$  each independently is -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>, -C<sub>3</sub>H<sub>7</sub>, -C<sub>4</sub>H<sub>9</sub>, -C<sub>5</sub>H<sub>11</sub>, -C<sub>6</sub>H<sub>13</sub>, -CH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>, -CH<sub>2</sub>phenyl, -C<sub>2</sub>H<sub>4</sub>phenyl, -C<sub>3</sub>H<sub>6</sub>phenyl, -C<sub>2</sub>H<sub>4</sub>CN, -C<sub>2</sub>H<sub>4</sub>OH, -C<sub>2</sub>H<sub>4</sub>OCH<sub>3</sub>, -C<sub>2</sub>H<sub>4</sub>COOCH<sub>3</sub>, -C<sub>4</sub>H<sub>8</sub>COCH<sub>3</sub>, -C<sub>2</sub>H<sub>4</sub>COCH<sub>3</sub>, -C<sub>2</sub>H<sub>4</sub>OCOCH<sub>3</sub>, -C<sub>3</sub>H<sub>6</sub>OCOCH<sub>3</sub>, -C<sub>4</sub>H<sub>8</sub>OCOCH<sub>3</sub>, -C<sub>2</sub>H<sub>4</sub>OC<sub>6</sub>H<sub>5</sub>, -C<sub>2</sub>H<sub>4</sub>OC<sub>6</sub>H<sub>4</sub>(SO<sub>2</sub>F), -C<sub>2</sub>H<sub>4</sub>COOC<sub>2</sub>H<sub>4</sub>OCH<sub>3</sub>, -C<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>COOC<sub>2</sub>H<sub>4</sub>OCH<sub>3</sub>, allyl, -C<sub>2</sub>H<sub>4</sub>Ophenyl, -C<sub>2</sub>H<sub>4</sub>O(fluorosulphonylphenyl), -CH<sub>2</sub>CH(CN)(OC<sub>2</sub>H<sub>5</sub>), C<sub>1-6</sub>-alkylphenylSO<sub>2</sub>F,



-COOC<sub>1-6</sub>-alkylOCOC<sub>1-6</sub>-alkyl or -COOC<sub>1-6</sub>-alkylCOOC<sub>1-6</sub>-alkyl

$R^3$  is -H, -OCH<sub>3</sub> or -Cl;

$R^4$  is -H, -CH<sub>3</sub>, -NHCOCH<sub>3</sub>, -NHCOC<sub>2</sub>H<sub>5</sub>, -NHCOCH(CH<sub>3</sub>)<sub>2</sub>, -NHCOC<sub>3</sub>H<sub>7</sub>Cl, -NHCOC(CH<sub>3</sub>)<sub>3</sub>, -OCH<sub>3</sub>, -OC<sub>4</sub>H<sub>9</sub>, -F, -Cl, -Br, -I or -NHSO<sub>2</sub>C<sub>1-6</sub>-alkyl;

$R^5$  is -H, -OCH<sub>3</sub>, -OC<sub>2</sub>H<sub>5</sub> or -Cl;

$R^6$  is -H, -CH<sub>3</sub>, -OCH<sub>3</sub>, -F, -Cl, Br, -I or -NHSO<sub>2</sub>C<sub>1-6</sub>-alkyl;

$R^{10}$  is -H, -OCH<sub>3</sub>, -NO<sub>2</sub>, -Cl, -Br or -CN;

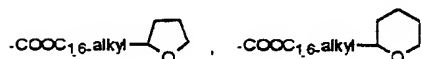
$R^{11}$  is -H;

$R^{12}$  is  $-\text{SO}_2\text{F}$  or  $-\text{NO}_2$ ;

$R^{13}$  is -H,  $-\text{OCH}_3$ ,  $-\text{SO}_2\text{F}$ , -Cl, -Br or  $-\text{NO}_2$ ; and

$R^{14}$  is -H,  $-\text{OCH}_3$ , -Cl, -Br or -CN, provided that at least one of  $R^3$  or  $R^5$  is -H and that at least one of  $R^4$  or  $R^6$  is -H.

More preferably compounds of Formula (4) are those in which  $R^1$  and  $R^2$  each independently is  $-\text{C}_2\text{H}_5$ ,  $-\text{C}_4\text{H}_9$ ,  $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ ,  $-\text{C}_2\text{H}_4\text{OCOCH}_3$ ,  $-\text{C}_4\text{H}_8\text{OCOCH}_3$ ,  $-\text{C}_2\text{H}_4\text{OCOPhenyl}$ ,  $-\text{CH}_2\text{phenyl}$ ,  $\text{C}_{1-6}\text{-alkylphenylSO}_2\text{F}$ ,  $\text{C}_{1-6}\text{-alkylOphenylSO}_2\text{F}$ ,



$-\text{COOC}_{1-6}\text{-alkylOCOC}_{1-6}\text{-alkyl}$  or  $-\text{COOC}_{1-6}\text{-alkylCOOC}_{1-6}\text{-alkyl}$

$R^4$  is -H,  $-\text{CH}_3$  or  $-\text{NHCOCH}_3$ ;

$R^3$ ,  $R^5$ ,  $R^6$  and  $R^{11}$  is -H;

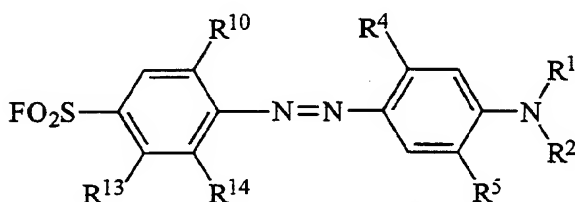
$R^{10}$  and  $R^{13}$  each independently is -H, -Cl, -Br or  $-\text{NO}_2$ ;

$R^{12}$  is  $-\text{SO}_2\text{F}$ ; and

$R^{14}$  is -H, -Cl or -Br.

An especially preferred compound of Formula (4) is that in which  $R^1$  is  $-\text{C}_2\text{H}_5$ ;  $R^2$  is  $-\text{C}_2\text{H}_4\text{OCOPhenyl}$ ;  $R^4$  is  $-\text{CH}_3$ ;  $R^{10}$  and  $R^{13}$  are both -Cl;  $R^{12}$  is  $-\text{SO}_2\text{F}$ ; and  $R^3$ ,  $R^5$ ,  $R^6$ ,  $R^{11}$  and  $R^{14}$  are all -H.

An especially preferred sub-group of compounds of Formula (1) are those of Formula (7):



Formula (7)

in which

$R^1$  and  $R^2$  each independently is optionally substituted  $\text{C}_{1-6}\text{-alkyl}$ ;

$R^4$  is alkyl or a group of Formula  $\text{R}^{19}\text{-N-Y-X-W}$

in which Y is a direct link or  $\text{C}=\text{O}$ , X is a direct link, alkyl, alkenyl, aryl, heterocyclic, alkylOalkyl,  $-\text{NR}^{20}\text{-Z-}$ ,  $-\text{COOZ}$  or  $-\text{O-Z}$  in which Z is alkyl, alkenyl, aryl, heterocyclic, alkylOalkyl or a direct link and  $R^{20}$

is -H, alkyl, aryl or alkylaryl, W is  $-\text{CO}_2\text{R}^{21}$ ,  $-\text{OCOR}^{21}$  or  $-\text{OH}$  in which  $\text{R}^{21}$  is alkyl, aryl, alkylaryl, alkylalkyl or alkylOH, and  $\text{R}^{19}$  is -H or alkyl;

$\text{R}^5$  is -H,  $\text{C}_{1-6}$ -alkoxy or -Ophenyl;

$\text{R}^{10}$  is  $-\text{NO}_2$  or  $-\text{Cl}$ ; and

$\text{R}^{13}$  and  $\text{R}^{14}$  each independently is -H or  $-\text{Cl}$ .

The dyes of Formula (7) are novel and form a further feature of the present invention.

In the dyes of Formula (7)

$\text{R}^1$  and  $\text{R}^2$  each independently is preferably  $\text{C}_{1-6}$ -alkyl or  $\text{C}_{1-6}$ -alkyl substituted by phenyl or  $-\text{COOC}_{1-6}$ -alkyl, and more preferably is ethyl, propyl, butyl, 1-methylpropyl, hexyl, benzyl, ethylphenyl or propylphenyl.

$\text{R}^4$  is preferably a group of Formula  $\text{R}^{19}-\text{N}-\text{Y}-\text{X}-\text{W}$  in which

$\text{R}^{19}$  is preferably -H or  $\text{C}_{1-6}$ -alkyl more preferably -H; Y is preferably a direct link or  $\text{C} = \text{O}$  more preferably  $\text{C} = \text{O}$ ;

X is preferably a direct link,  $\text{C}_{1-8}$ -alkyl,  $\text{C}_{2-8}$ -alkenyl, any of the carbocyclic or heterocyclic groups defined above for A,  $\text{C}_{1-6}$ -alkylOC $_{1-6}$ -alkyl,  $-\text{NR}^{20}-\text{Z}-$ ,  $-\text{COOZ}$  or  $-\text{O}-\text{Z}-$  in which  $\text{R}^{20}$  is preferably -H,  $\text{C}_{1-6}$ -alkyl, phenyl or benzyl and

Z is preferably a direct link or  $\text{C}_{1-6}$ -alkyl,  $\text{C}_{2-8}$ -alkenyl, phenyl, benzyl or any of the heterocyclic groups defined above for A;

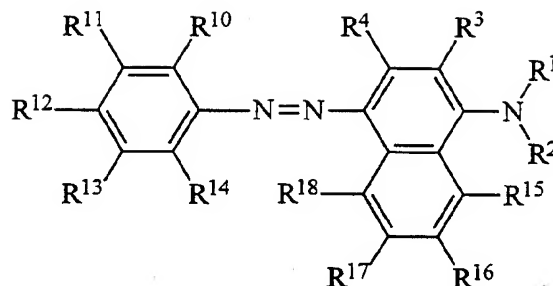
X is more preferably a direct link,  $\text{CH}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CH}_2\text{C}(\text{CH}_3)_2$ , cyclohexyl,  $\text{CH} = \text{CH}$ , phenyl,  $-\text{NR}^{20}-\text{Z}$ ,  $-\text{COOZ}$  or  $-\text{O}-\text{Z}-$  in which

$\text{R}^{20}$  is preferably -H, Z is preferably a direct link,  $\text{C}_{1-6}$ -alkyl or benzyl.

W is  $-\text{CO}_2\text{R}^{21}$ ,  $-\text{OCOR}^{21}$  or  $-\text{OH}$  in which  $\text{R}^{21}$  is  $\text{C}_{1-6}$ -alkyl, phenyl, chlorobenzyl,  $\text{C}_{1-6}$ -alkoxybenzyl, benzyl,  $\text{C}_{1-6}$ -alkylOC $_{1-6}$ -alkyl or  $\text{C}_{1-6}$ -alkylOH more preferably ethyl, methyl, butyl, or 1,3-dimethylbutyl.

Dyes in which both A and D are phenyl and in which one of A and D carries a 4- $\text{SO}_2\text{F}$  group are generally more stable and build up better on polyester textile material than do the corresponding 2- $\text{SO}_2\text{F}$  dyes.

A further preferred sub-group of compounds of Formula (1) are those of Formula (5);



Formula (5)

wherein:

$R^1$  to  $R^4$  and  $R^{10}$  to  $R^{14}$  are as herein before defined; and

$R^{15}$  to  $R^{18}$  each independently is -H, -F, -Cl, -Br, -I, -SO<sub>2</sub>F, -NO<sub>2</sub>,  
-CN, -NR<sub>1</sub>R<sub>2</sub>, OH or optionally substituted -C<sub>1-6</sub>-alkyl or  
-C<sub>1-6</sub>-alkoxy.

The optional substituents for any of the groups represented  
by  $R^{15}$  to  $R^{18}$  may be selected from any of optional substituents described  
above for A, D,  $R^1$  and  $R^2$ .

Compositions comprising dispersions of the compounds of  
Formula (1) in which A is an optionally substituted heterocyclic or  
carbocyclic group; and D is an optionally substituted carbocyclic group;  
and at least one of A or D carries directly at least one -SO<sub>2</sub>F group or  
carried a substituent to which at least one -SO<sub>2</sub>F group is attached in  
aqueous media are novel and form a further feature of the present  
invention. Compositions comprising dispersions of compounds of Formulae  
(2), (3), (4), (5) and (7) are also novel. The compositions typically  
comprise from 1% to 30% of a compound of Formulae (1), (2), (3), (4), (5)  
or (6) in an aqueous medium. The compositions are preferably buffered at  
pH 2 to 7 more preferably at pH 4 to 6.

These dispersions may further comprise ingredients  
conventionally used in dyeing applications such as dispersing agents for  
example lignosulphonates, naphthalene sulphonic acid/formaldehyde  
condensates or phenol/cresol/sulphanilic acid/formaldehyde condensates,  
surfactants, wetting agents such as alkyl aryl ethoxylates which may be  
sulphonated or phosphated, inorganic salts, de-foamers such as mineral  
oil or nonanol, organic liquids and buffers. Dispersing agents may be  
present at from 10% to 200% on the weight of the compound of Formulae  
(1), (2), (3), (4), (5) or (7). Wetting agents may be used at from 0% to  
20% on the weight of the compound (1), (2), (3), (4), (5) or (7). The  
dispersions may be prepared by bead milling the compound of Formula (1),

(2), (3), (4), (5) or (7) with glass beads or sand in an aqueous medium.

According to a further feature of the present invention there is provided a process for the mass coloration of plastics which comprises incorporating into a plastics material a compound or mixture thereof which is free from water solubilising groups, of Formula (1) wherein A and D each independently is an optionally substituted heterocyclic or carbocyclic group and at least one of A or D carries directly at least one  $-SO_2F$  group or carries a substituent to which at least one  $-SO_2F$  group is attached.

According to a further feature of the present invention there is provided a process for the mass coloration of plastics which comprises incorporating into a plastics material a compound or mixture thereof which is free from water solubilising groups, of Formula (1) wherein A and D each independently is an optionally substituted heterocyclic or carbocyclic group and at least one of A or D carries directly at least one  $-SO_2F$  group or carries a substituent to which at least one  $-SO_2F$  group is attached and at least one of A or D carries directly at least one ester group or carries a substituent to which at least one ester group is attached.

The plastics may be selected from polystyrene, acrylics, styrene/acrylonitrile mixtures, acrylonitrile/butadiene/styrene mixtures, polycarbonate, polyether-sulphone, nylons, rigid PVC (uPVC) and polypropylene.

The compound may be incorporated by blending with granules or powdered plastics material by, for example, dry tumbling or high-speed mixing followed by injection moulding on a screw machine or by conventional compounding/masterbatching techniques. The present dyes generally dissolve or disperse readily in hot plastics melt and provide bright coloration generally with good clarity and good light fastness.

The plastics materials when coloured with the above dyes form a further feature of the present invention.

The compounds of Formula (1) may be obtained by usual methods for the preparation of azo compounds such as by diazotisation of an amine of Formula  $A-NH_2$  or  $A^1-NH_2$  and coupling onto a component  $D-X$  or  $D^1-X$  in which A,  $A^1$ , D and  $D^1$  are as hereinbefore defined and X is a group displaceable by a diazotised amine. Typically the amine,  $A-NH_2$  or  $A^1-NH_2$ , may be diazotised in an acidic medium, such as acetic, propionic or hydrochloric acid using a nitrosating agent such as nitrosylsulphuric acid, sodium nitrite or methyl nitrite at a temperature from  $-10^\circ C$  to  $10^\circ C$ . Coupling onto the component  $D-X$  or  $D^1-X$  may be achieved by adding the diazotised amine to a mixture of  $D-X$  or  $D^1-X$  in an alkanol such as methanol at a temperature from  $0^\circ C$  to  $10^\circ C$ . After coupling the compound of Formula (1) may be recovered from the reaction mixture by any convenient means such as by filtration.

Fluorosulphonyl groups may be introduced into the compounds of Formula (1) or Formula (2) or into the A, A<sup>1</sup>, D and D<sup>1</sup> components prior to coupling by methods generally available in the literature. For example reaction of the compound of Formula (1) or Formula (2), A-NH<sub>2</sub>, A<sup>1</sup>-NH<sub>2</sub>, the NH<sub>2</sub> being protected as necessary, D-X or D<sup>1</sup>-X, in which A, A<sup>1</sup>, D and D<sup>1</sup> are as hereinbefore defined, with chlorosulphonic acid optionally in the presence of dimethylformamide and thionylchloride at a temperature of from 30°C to 140°C gives the chlorosulphonyl derivative. The chlorosulphonyl derivative may be reacted in boiling aqueous media with potassium fluoride to give the fluorosulphonyl derivative.

Alternatively the compound of Formula (1) or Formula (2), A-NH<sub>2</sub>, A<sup>1</sup>-NH<sub>2</sub>, D-X or D<sup>1</sup>-X may be sulphonated with sulphuric acid or oleum to give the sulphonic acid derivative which may be converted to the chlorosulphonyl derivative by reaction, either of the free acid or an inorganic salt thereof, with thionylchloride optionally in the presence of a chlorophosphorus compound such as phosphorus oxychloride or phosphorus pentachloride in an organic liquid such as an aromatic hydrocarbon at a temperature of from 20°C to 110°C. Similarly a sulphonate ester may be converted to the corresponding chlorosulphonyl derivative. The chlorosulphonyl derivative may then be converted to the fluorosulphonyl derivative as described above.

The compounds of Formulae (1), (2), (3), (4), (5) and (7) are useful for the coloration of synthetic textile materials particularly polyester textile materials and fibre blends thereof to which they impart colours which have excellent wet and light fastness properties.

The compounds of Formula (1), (2), (3), (4), (5) or (7) are also useful for the mass coloration of plastics as described above and impart bright colours generally with good clarity and light fastness.

The invention is further illustrated by the following Examples.

#### Example 1

##### Preparation of 4-(2,5-dichloro-4-fluorosulphonylphenylazo)-3-methyl-N-ethyl-N-(2-benzoyloxyethyl)aniline

##### i) Preparation of 2,5-dichloro-4-chlorosulphonylaniline

2,5-Dichloroaniline (32.4 parts) was added portionwise to chlorosulphonic acid (93 parts) at 35°C. The mixture was stirred at 120°C for 3hrs and then cooled to 70°C. Dimethyl formamide (1.6 parts) and thionyl chloride (15 parts) were added, maintaining the temperature at 65-70°C and the mixture stirred at 70°C for 24 hours. The reaction mixture was cooled to ambient temperature and poured with caution onto stirred ice (1000 parts) producing a cream precipitate. The product was isolated by filtration, washed acid-free with ice/water and dried under vacuum to yield; 2,5-dichloro-4-chlorosulphonylaniline (44.2 parts).

##### ii) Preparation of 2,5-dichloro-4-fluorosulphonylaniline

A mixture of 2,5-dichloro-4-chlorosulphonylaniline (44.2



parts), potassium fluoride (38 parts) and water (100 parts) was stirred under reflux for 5 hours. The reaction mixture was cooled to ambient temperature and drowned into water (300 parts). The cream precipitate was isolated by filtration, washed with water and dried under vacuum to yield; 2,5-dichloro-4-fluorosulphonylaniline (37.2 parts).

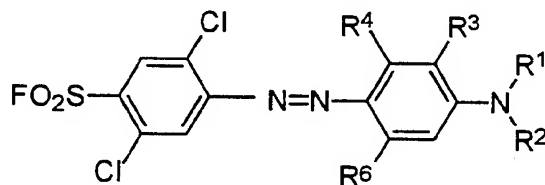
iii) Preparation of 3-methyl-N-ethyl-N-(2-benzoyloxyethyl)aniline

Benzoylchloride (3.3g) was added to a mixture of N-ethyl-N-hydroxyethyl-3-methylaniline (2.1g) in acetone (25cm<sup>3</sup>) and pyridine (1cm<sup>3</sup>) and stirred at reflux for 1 hour. The reaction mixture was cooled and used directly in iv) below.

iv) Preparation of 4-(2,5-dichloro-4-fluorosulphonylphenylazo)-3-methyl-N-ethyl-N-(2-benzoyloxyethyl)aniline

Nitrosyl sulphuric acid (3cm<sup>3</sup> of 40%) was added to a mixture of 2,5-dichloro-4-fluorosulphonylaniline (2g) in acetic/propionic acid (86:14, 25cm<sup>3</sup>) at 0°C to 5°C. The mixture was stirred at 0°C to 5°C for 2 hours before adding the reaction mixture from iii) above in methanol (100cm<sup>3</sup>) at 0°C to 5°C. The precipitated solid was collected by filtration, washed with water, slurried with methanol, collected by filtration and washed with methanol to give 4-(2,5-dichloro-4-fluorosulphonylphenylazo)-3-methyl-N-ethyl-N-(2-benzoyloxyethyl)aniline (2.1g) when applied to polyester materials from aqueous dispersion gives bluish-red shades with excellent wet and light fastness properties.

The following examples of dyes of Formula:



were prepared by the procedure of Example 1:

Ex	R <sup>1</sup>	R <sup>2</sup>	R <sup>4</sup>	R <sup>3</sup>	R <sup>6</sup>	$\lambda_{\text{max}}$ /nm
2	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OH	-NHCOCH <sub>3</sub>	-H	-H	522
3	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-NHCOCH <sub>3</sub>	-H	-H	518
4	-CH <sub>2</sub> CH=CH <sub>2</sub>	-CH <sub>2</sub> CH=CH <sub>2</sub>	-NHCOCH <sub>3</sub>	-H	-H	520
5	-C <sub>4</sub> H <sub>8</sub> OCOCH <sub>3</sub>	-C <sub>4</sub> H <sub>8</sub> OCOCH <sub>3</sub>	-NHCOCH <sub>3</sub>	-H	-H	535
6	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-NHCOCH <sub>3</sub>	-H	-H	504
7	-C <sub>2</sub> H <sub>4</sub> COOCH <sub>3</sub>	-C <sub>2</sub> H <sub>4</sub> COOCH <sub>3</sub>	-NHCOCH <sub>3</sub>	-H	-H	509
8	-C <sub>4</sub> H <sub>9</sub>	-C <sub>2</sub> H <sub>4</sub> COOCH <sub>3</sub>	-NHCOCH <sub>3</sub>	-H	-H	528
9	-C <sub>4</sub> H <sub>9</sub>	-C <sub>2</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	-NHCOCH <sub>3</sub>	-H	-H	530
10	-C <sub>2</sub> H <sub>4</sub> COOCH <sub>3</sub>	-C <sub>4</sub> H <sub>8</sub> OCOCH <sub>3</sub>	-NHCOCH <sub>3</sub>	-H	-H	526
11	-C <sub>2</sub> H <sub>4</sub> OH	-C <sub>2</sub> H <sub>4</sub> OH	-CH <sub>3</sub>	-H	-H	508
12	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-H	-OCH <sub>3</sub>	-H	518
13	-C <sub>2</sub> H <sub>4</sub> CN	-H	-H	-OCH <sub>3</sub>	-CH <sub>3</sub>	504
14	-C <sub>2</sub> H <sub>4</sub> CN	-H	-CH <sub>3</sub>	-H	-H	464
15	-C <sub>2</sub> H <sub>4</sub> CN	-H	-H	-Cl	-H	440
16	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-Cl	-H	-H	470
17	-C <sub>4</sub> H <sub>8</sub> OCOCH <sub>3</sub>	-C <sub>4</sub> H <sub>8</sub> OCOCH <sub>3</sub>	-CH <sub>3</sub>	-H	-CH <sub>3</sub>	512
18	-C <sub>2</sub> H <sub>4</sub> CN	-C <sub>2</sub> H <sub>4</sub> CN	-CH <sub>3</sub>	-H	-CH <sub>3</sub>	465
19	-C <sub>2</sub> H <sub>4</sub> CN	-C <sub>2</sub> H <sub>4</sub> COOCH <sub>3</sub>	-H	-H	-H	460
20	-C <sub>2</sub> H <sub>5</sub>	-C <sub>4</sub> H <sub>8</sub> OCOCH <sub>3</sub>	-CH <sub>3</sub>	-H	-H	530
21	-C <sub>4</sub> H <sub>8</sub> OCOCH <sub>3</sub>	-C <sub>4</sub> H <sub>8</sub> OCOCH <sub>3</sub>	-CH <sub>3</sub>	-H	-H	502
22	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-C <sub>2</sub> H <sub>4</sub> OCOC <sub>2</sub> H <sub>5</sub>	-H	-OCH <sub>3</sub>	-NHCOCH <sub>3</sub>	548
23	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OH	-CH <sub>3</sub>	-H	-H	520
24	-C <sub>2</sub> H <sub>5</sub>	-C <sub>4</sub> H <sub>8</sub> OH	-CH <sub>3</sub>	-H	-H	530

Ex	R <sup>1</sup>	R <sup>2</sup>	R <sup>4</sup>	R <sup>3</sup>	R <sup>6</sup>	$\lambda_{max}/n_m$
25	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> CH(OH)C <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-H	-H	532
26	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-H	-OCH <sub>3</sub>	-CH <sub>3</sub>	548
27	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> C(OH)(OC <sub>2</sub> H <sub>5</sub> )	-CH <sub>3</sub>	-H	-H	525
28	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> C(OH)(CN)	-CH <sub>3</sub>	-H	-H	523
29	-C <sub>5</sub> H <sub>11</sub>	-C <sub>2</sub> H <sub>4</sub> OH	-CH <sub>3</sub>	-H	-H	529
30	-C <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	-C <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	-CH <sub>3</sub>	-H	-H	520
31	-C <sub>4</sub> H <sub>9</sub>	-C <sub>2</sub> H <sub>4</sub> OH	-CH <sub>3</sub>	-H	-H	528
32	-C <sub>6</sub> H <sub>13</sub>	-C <sub>2</sub> H <sub>4</sub> OH	-CH <sub>3</sub>	-H	-H	531
33	-C <sub>2</sub> H <sub>4</sub> Ophenyl	-C <sub>2</sub> H <sub>4</sub> OH	-CH <sub>3</sub>	-H	-H	520
34	-CH <sub>2</sub> C(CN)(OC <sub>2</sub> H <sub>5</sub> )	-CH <sub>2</sub> C(CN)(OC <sub>2</sub> H <sub>5</sub> )	-CH <sub>3</sub>	-H	-H	517
35	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	-CH <sub>3</sub>	-H	-H	525
36	-CH <sub>3</sub>	-CH <sub>3</sub>	-H	-H	-H	515
37	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-H	-H	-H	520
38	-C <sub>3</sub> H <sub>7</sub>	-C <sub>3</sub> H <sub>7</sub>	-H	-H	-H	522
39	-C <sub>4</sub> H <sub>9</sub>	-C <sub>4</sub> H <sub>9</sub>	-H	-H	-H	527
40	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-NHCOCH <sub>3</sub>	-H	-H	536
41	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OCOPhenyl	-CH <sub>3</sub>	-H	-H	514
42	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-H	-H	514
43	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	-CH <sub>3</sub>	-H	-H	513
44	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>4</sub> OC <sub>4</sub> H <sub>9</sub>	-CH <sub>3</sub>	-H	-H	513
45	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOCH <sub>2</sub> tetrahydrofuran-2-yl	-CH <sub>3</sub>	-H	-H	512
46	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>4</sub> Ophenyl	-CH <sub>3</sub>	-H	-H	512
47	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOCH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-H	-H	511

Ex	R <sup>1</sup>	R <sup>2</sup>	R <sup>4</sup>	R <sup>3</sup>	R <sup>6</sup>	$\lambda_{max}/n_m$
48	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	-CH <sub>3</sub>	-H	-H	513
49	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-H	-H	513
50	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-H	-H	512
51	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOCH(CH <sub>3</sub> ) <sub>2</sub>	-CH <sub>3</sub>	-H	-H	513
52	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>4</sub> OH	-CH <sub>3</sub>	-H	-H	514
53	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOCH <sub>2</sub> tetrahydropyran-2-yl	-CH <sub>3</sub>	-H	-H	512
54	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOCH <sub>2</sub> phenyl	-CH <sub>3</sub>	-H	-H	513
55	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOC <sub>3</sub> H <sub>5</sub> COOC <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-H	-H	514
56	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOCH(C <sub>2</sub> H <sub>5</sub> )COOC <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-H	-H	514
57	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOC <sub>4</sub> H <sub>9</sub> OH	-CH <sub>3</sub>	-H	-H	514
58	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOC <sub>4</sub> H <sub>9</sub> OCOCH <sub>3</sub>	-CH <sub>3</sub>	-H	-H	513
59	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOCH <sub>2</sub> COOCH <sub>3</sub>	-CH <sub>3</sub>	-H	-H	511
60	-C <sub>2</sub> H <sub>4</sub> OH	-C <sub>2</sub> H <sub>4</sub> COOCH <sub>2</sub> tetrahydrofuran-2-yl	-CH <sub>3</sub>	-H	-H	511
61	-C <sub>2</sub> H <sub>4</sub> OH	-C <sub>2</sub> H <sub>4</sub> COOCH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-H	-H	510
62	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOCH <sub>2</sub> CN	-CH <sub>3</sub>	-H	-H	512
63	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>4</sub> CN	-CH <sub>3</sub>	-H	-H	514
64	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> COOCH <sub>2</sub> COCH <sub>3</sub>	-CH <sub>3</sub>	-H	-H	513
65	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OCOC(CH <sub>3</sub> ) <sub>3</sub>	-CH <sub>3</sub>	-H	-H	511
66	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OCO(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	-CH <sub>3</sub>	-H	-H	510
67	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OCOCH(CH <sub>3</sub> ) <sub>2</sub>	-CH <sub>3</sub>	-H	-H	510
68	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OCO(CH <sub>2</sub> ) <sub>3</sub> Cl	-CH <sub>3</sub>	-H	-H	507
69	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OCO(4-NO <sub>2</sub> phenyl)	-CH <sub>3</sub>	-H	-H	503
70	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OCO(4-CH <sub>3</sub> phenyl)	-CH <sub>3</sub>	-H	-H	511

Ex	R <sup>1</sup>	R <sup>2</sup>	R <sup>4</sup>	R <sup>3</sup>	R <sup>5</sup>	$\lambda_{max}/nm$
71	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OCO(3-CH <sub>3</sub> phenyl)	-CH <sub>3</sub>	-H	-H	511
72	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> O(4-OCH <sub>3</sub> phenyl)	-CH <sub>3</sub>	-H	-H	512
73	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> O(2-OCH <sub>3</sub> phenyl)	-CH <sub>3</sub>	-H	-H	509
74	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-H	-H	521
75	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>4</sub> COOCH <sub>3</sub>	-CH <sub>3</sub>	-H	-H	521
76	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>4</sub> COOCH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-H	-H	521
77	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OCOC <sub>2</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-H	-H	511
78	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>2</sub> Ophenyl	-CH <sub>3</sub>	-H	-H	515
79	-C <sub>2</sub> H <sub>4</sub> OH	-C <sub>2</sub> H <sub>4</sub> OCophenyl	-CH <sub>3</sub>	-H	-H	517
80	-C <sub>2</sub> H <sub>4</sub> COOC <sub>3</sub> H <sub>7</sub>	-C <sub>2</sub> H <sub>4</sub> COOC <sub>3</sub> H <sub>7</sub>	-NHCOCH <sub>3</sub>	-H	-H	498
81	-C <sub>2</sub> H <sub>5</sub>	-C <sub>3</sub> H <sub>6</sub> COOC <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-H	-H	523
82	-cyclohexyl	-CH <sub>2</sub> phenyl	-H	-H	-H	509
83	-C <sub>4</sub> H <sub>9</sub>	-CH(CH <sub>3</sub> ) <sub>2</sub>	-NHCOCH <sub>3</sub>	-H	-H	539
84	-C <sub>2</sub> H <sub>5</sub>	-C <sub>4</sub> H <sub>9</sub>	-NHCOCH <sub>3</sub>	-H	-H	539
85	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	-CH <sub>3</sub>	-H	-H	525
86	-C <sub>2</sub> H <sub>4</sub> OH	-C <sub>2</sub> H <sub>4</sub> Ophenyl	-CH <sub>3</sub>	-H	-H	520

Example 87Preparation of 4-(2,6-dibromo-4-fluorosulphonylphenylazo)-3-acetamido-N,N-diethylanilinei) Preparation of 2,6-dibromo-4-fluorosulphonylaniline

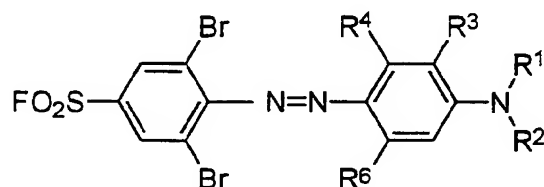
To a solution of 4-aminobenzenesulphonyl fluoride (10 parts) in acetic acid (100 parts), stirring at 0-5°C, was added gradually a solution of bromine (18 parts) in acetic acid (50 parts); keeping the temperature below 5°C. The temperature was allowed to warm to ambient and the mixture was stirred at this temperature for a further 1hr. The reaction mass was drowned into water (500 parts), the product was isolated by filtration, washed with cold water and dried at 50°C to yield; 2,6-dibromo-4-fluorosulphonylaniline (17.5 parts).

ii) Preparation of 4-(2,6-dibromo-4-fluorosulphonylphenylazo)-3-acetamido-N,N-diethylaniline

A mixture of 2,6-dibromo-4-fluorosulphonylaniline (2.7 parts) and acetic/propionic acid mixture (15 parts, 86/14 vol/vol) was stirred and heated until a complete solution was formed. The solution was set stirring at 0-5°C, and nitrosyl sulphuric acid soln (5 parts) was added dropwise. The mixture was stirred at this temperature for a further 30min.

The diazo solution was added slowly to a mixture of 3-N,N-diethylaminoacetanilide (1.7 parts), methanol (50 parts) and sulphamic acid (0.5 parts); stirring at 0-5°C. After stirring for 1hr at this temperature, water (50 parts) was added and the mixture was stirred a further 30min at ambient temperature. The product was isolated by filtration, washed with water and methanol and then dried at 50°C to yield; 4-(2,6-dibromo-4-fluorosulphonylphenylazo)-3-acetamido-N,N-diethylaniline (1.8 parts)  $\lambda_{\max}=480\text{nm}$ .

When applied to polyester materials from an aqueous dispersion, the dye gives dull orange shades with excellent light fastness and excellent fastness to wet treatments. The following examples of dyes of Formula:



were prepared by the procedure of Example 87:

Ex	R <sup>1</sup>	R <sup>2</sup>	R <sup>4</sup>	R <sup>3</sup>	R <sup>6</sup>	$\lambda_{\max}$ /nm
88	-C <sub>2</sub> H <sub>4</sub> OH	-C <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub>	-H	-H	-H	434
89	-C <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	-C <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	-CH <sub>3</sub>	-H	-H	447
90	-C <sub>2</sub> H <sub>4</sub> CN	-C <sub>2</sub> H <sub>4</sub> CN	-CH <sub>3</sub>	-H	-H	418
91	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> CN	-CH <sub>3</sub>	-H	-H	435
92	-H	-C <sub>2</sub> H <sub>4</sub> CN	-H	-H	-H	399
93	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> CN	-H	-H	-H	421
94	-C <sub>2</sub> H <sub>4</sub> OH	-C <sub>2</sub> H <sub>4</sub> CN	-H	-H	-H	420
95	-C <sub>2</sub> H <sub>4</sub> CN	-C <sub>2</sub> H <sub>4</sub> CN	-H	-H	-H	406
96	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-H	-H	-H	438
97	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-H	-H	453
98	-C <sub>2</sub> H <sub>4</sub> OH	-C <sub>2</sub> H <sub>4</sub> OH	-CH <sub>3</sub>	-H	-H	454
99	-C <sub>4</sub> H <sub>9</sub>	-C <sub>4</sub> H <sub>9</sub>	-H	-H	-H	442
100	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> phenyl	-H	-H	-H	431
101	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-NHCOCH <sub>3</sub>	-H	-H	486
102	-C <sub>4</sub> H <sub>9</sub>	-C <sub>4</sub> H <sub>9</sub>	-NHCOCH <sub>3</sub>	-H	-H	486
103	-C <sub>4</sub> H <sub>9</sub> OCOCH <sub>3</sub>	-C <sub>4</sub> H <sub>9</sub> OCOCH <sub>3</sub>	-NHCOCH <sub>3</sub>	-H	-H	479

Example 104Preparation of 4-(2,6-dicyano-4-fluorosulphonylphenylazo)-3-acetamido-N,N-diethylaniline

A mixture of 4-(2,6-dibromo-4-fluorosulphonylphenylazo)-3-acetamido-N,N-diethylaniline (Example 101) (1.5 parts), cuprous cyanide (0.54 parts) and dimethylformamide (20 parts) was stirred at ambient temperature for 3hr. The reaction mixture was diluted with water (40 parts), stirred for 30min and the product was isolated by filtration to yield; 4-(2,6-dicyano-4-fluorosulphonylphenylazo)-3-acetamido-N,N-diethylaniline (0.8 parts)  $\lambda_{\max}=611\text{nm}$ .

When applied to polyester materials from an aqueous dispersion, the dye gives bright blue shades with excellent light fastness and excellent fastness to wet treatments.

Example 105Preparation of 4-(2,6-dicyano-4-fluorosulphonylphenylazo)-3-acetamido-N,N-di-n-butyl aniline

The dye in Example 102 (3.0g) was stirred in DMF (30cm<sup>3</sup>) and CuCN (1.0g) at 90°C for 2 hours. The reaction mix was drowned onto ice and the precipitate collected, washed with water and dried under suction. The filter cake was dissolved in dichloromethane, filtered and the filtrate evaporated to give a blue dye ( $\lambda_{\max}$  611nm).

Example 106Preparation of 4-(2,6-dicyano-4-fluorosulphonylphenylazo)-3-acetamido-N,N-diacetoxylbutylamino aniline

The dye in Example 103 (3.0g) was stirred in DMF (30cm<sup>3</sup>) and CuCN (1.0g) at 90°C for 2 hours. The reaction mix was drowned onto ice and the precipitate collected, washed with water and dried under suction. The filter cake was dissolved in dichloromethane, filtered and the filtrate evaporated to give a blue dye ( $\lambda_{\max}$  608nm).

Example 107Preparation of 4-(2,6-dichloro-4-fluorosulphonylphenylazo)-N,N-di-n-butylanilinei) Preparation of 2,6-dichloro-4-chlorosulphonylaniline

The procedure of Example 1ii) was repeated except that in place of the 32.4 parts of 2,5-dichloroaniline, 32.4 parts of 2,6-dichloroaniline were used, to yield 2,6-dichloro-4-chlorosulphonylaniline (42.6 parts).

ii) Preparation of 2,6-dichloro-4-fluorosulphonylaniline

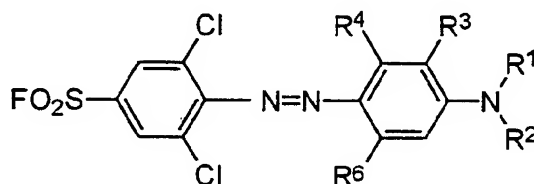
The procedure of Example 1ii) was repeated except that in place of the 44.2 parts of 2,5-dichloro-4-chlorosulphonylaniline, 42.6 parts of 2,6-dichloro-4-chlorosulphonylaniline were used, to yield 2,6-dichloro-4-fluorosulphonylaniline (36.0 parts).

iii) Preparation of 4-(2,6-dichloro-4-fluorosulphonylphenylazo)-N,N-di-n-butylaniline

A mixture of 2,6-dichloro-4-fluorosulphonylaniline (2.0

parts) and acetic/propionic acid mixture (15 parts, 86/14 vol/vol) was stirred and heated until a complete solution was formed. The solution was set stirring at 0-5°C and nitrosyl sulphuric acid solution (5 parts) was added slowly. The mixture was stirred at this temperature for a further 30min. The cooled diazo solution was added slowly to a mixture of N,N-di-n-butylaniline (1.7 parts), methanol (40 parts) and sulphamic acid (0.5 parts); stirring at 0-5°C. After stirring for 3hr at this temperature, water (50 parts) was added and the mixture stirred for a further 2hr at ambient. The product was isolated by filtration, washed with water and methanol and dried to yield; 4-(2,6-dichloro-4-fluorosulphonylphenylazo)-N,N-di-n-butylaniline (3.0 parts)  $\lambda_{\max}=443\text{nm}$ . When applied to polyester materials from an aqueous dispersion, the dye gives dull yellow brown shades with excellent fastness to light and wet treatments.

The following examples of dyes of Formula:



were prepared by the procedure of Example 107:

Example	R <sup>1</sup>	R <sup>2</sup>	R <sup>6</sup>	R <sup>3</sup>	R <sup>6</sup>	$\lambda_{\max}/\text{nm}$
108	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-H	-H	-H	439
109	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-H	-H	455
110	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> phenyl	-H	-H	-H	431

#### Example 111

##### Preparation of 4-(2-bromo-4-fluorosulphonylphenylazo)-3-acetamido-N,N-diethylaniline

The procedure of Example 87ii) was repeated except that in place of the 2.7 parts of 2,6-dibromo-4-fluorosulphonylaniline; 2.0 parts of 2-bromo-4-fluorosulphonylaniline were used. The product, 4-(2-bromo-4-fluorosulphonylphenylazo)-3-acetamido-N,N-diethylaniline (1.6 parts)  $\lambda_{\max}=524\text{nm}$ , when applied to polyester materials from an aqueous dispersion gives bright mid red shades with excellent fastness to light and wet treatments.



Example 112Preparation of 4-(2,5-dimethoxy-4-fluorosulphonylphenylazo)-3-acetamido-N,N-diethylaniline

The procedure of Example 87ii) was repeated except that in place of the 2.7 parts of 2,6-dibromo-4-fluorosulphonylaniline; 1.9 parts of 2,5-dimethoxy-4-fluorosulphonylaniline were used. The product, 4-(2,5-dimethoxy-4-fluorosulphonylphenylazo)-3-acetamido-N,N-diethylaniline (1.4 parts)  $\lambda_{\text{max}}=545\text{nm}$ , when applied to polyester materials from an aqueous dispersion gives bluish red shades with excellent fastness to light and wet treatments.

Example 113Preparation of 4-(2-nitro-5-chloro-4-fluorosulphonylphenylazo)-3-acetamido-N,N-diethylaniline

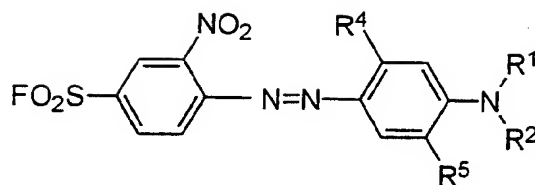
The procedure of Example 87ii) was repeated except that in place of the 2.7 parts of 2,6-dibromo-4-fluorosulphonylaniline; 2.0 parts of 2-nitro-5-chloro-4-fluorosulphonylaniline were used. The product, 4-(2-nitro-5-chloro-4-fluorosulphonylphenylazo)-3-acetamido-N,N-diethylaniline (2.6 parts)  $\lambda_{\text{max}}=550\text{nm}$ , when applied to polyester materials from an aqueous dispersion gives bluish red shades with excellent fastness to light and wet treatments.

Example 114i) Preparation of 2-nitro-4-fluorosulphonylaniline

N-acetyl sulphanilyl chloride (100g) was dissolved in concentrated sulphuric acid (515 cm<sup>3</sup>), cooled to 4°C and a mixture of concentrated nitric acid (38.6 cm<sup>3</sup>) and concentrated sulphuric acid (42.9 cm<sup>3</sup>) added dropwise maintaining the temperature at 4-6°C. After 1 hour the reaction mix was drowned onto ice and the precipitate collected, extracted into dichloromethane and evaporated to a yellow solid (92g). 31g of this yellow solid was refluxed for 3 hours in water (20 cm<sup>3</sup>), p-dioxane (20 cm<sup>3</sup>) and KF (19.4g) then drowned onto ice and the precipitate collected. This precipitate was refluxed in absolute ethanol (35 cm<sup>3</sup>) and concentrated hydrochloric acid (35 cm<sup>3</sup>) for 1 hour then drowned onto ice, filtered and suction dried. Recrystallisation from ethanol yielded 8.7g of the required compound.

ii) 2-Nitro-4-fluorosulphonyl aniline (0.01 mol) was dispersed in a mixture of acetic:propionic acid (86:14; 25cm<sup>3</sup>), cooled to 0-5°C and nitrosyl sulphuric acid (0.01 mol) added portionwise at 0-5°C. The reaction mixture was stirred for 10 minutes at 0-5°C then added dropwise to a mixture of the 3-(N,N-diethylamino) acetanilide (0.01mol), methanol (50cm<sup>3</sup>) and ice (50g). The resultant precipitate was filtered, washed with water and then methanol and oven dried at 50°C. The dry dye has a  $\lambda_{\text{max}}$  of 541nm and gives good fastness to washing, light and heat.

The following examples of dyes of Formula:



were prepared by the procedure of Example 114:

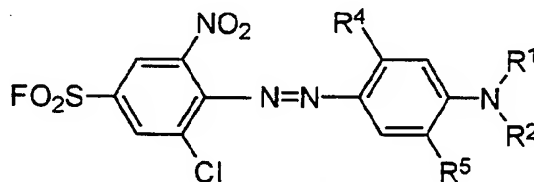
Example	R <sup>4</sup>	R <sup>1</sup>	R <sup>2</sup>	R <sup>5</sup>	$\lambda_{\max}$ (nm)
115	-NHCOCH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-H	541
116	-NHCOCH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-OCH <sub>3</sub>	590
117	-NHCOCH <sub>3</sub>	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-OCH <sub>3</sub>	564
118	-CH <sub>3</sub>	-C <sub>4</sub> H <sub>8</sub> OCOCH <sub>3</sub>	-C <sub>4</sub> H <sub>8</sub> OCOCH <sub>3</sub>	-H	530
119	-NHCOCH <sub>3</sub>	-C <sub>4</sub> H <sub>9</sub>	-CH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub>	-H	546
120	-NHCOCH <sub>3</sub>	-C <sub>4</sub> H <sub>9</sub>	-C <sub>4</sub> H <sub>9</sub>	-OCH <sub>3</sub>	591
121	-NHCOCH <sub>3</sub>	-C <sub>5</sub> H <sub>11</sub>	-C <sub>5</sub> H <sub>11</sub>	-OCH <sub>3</sub>	593
122	-NHCOC <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-OCH <sub>3</sub>	592
123	-NHCOC <sub>3</sub> H <sub>7</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-OCH <sub>3</sub>	592
124	-NHCOCH(CH <sub>3</sub> ) <sub>2</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-OCH <sub>3</sub>	591
125	-NHCOC <sub>4</sub> H <sub>9</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-OCH <sub>3</sub>	593
126	-OC <sub>4</sub> H <sub>9</sub>	-C <sub>4</sub> H <sub>9</sub>	-C <sub>4</sub> H <sub>9</sub>	-OCH <sub>3</sub>	575
127	-HNCOCCH <sub>3</sub>	-C <sub>3</sub> H <sub>7</sub>	-C <sub>3</sub> H <sub>7</sub>	-OCH <sub>3</sub>	594
128	-HNSO <sub>2</sub> CH <sub>3</sub>	-C <sub>3</sub> H <sub>7</sub>	-C <sub>3</sub> H <sub>7</sub>	-OCH <sub>3</sub>	562
129	-HNCOCCH(CH <sub>3</sub> ) <sub>2</sub>	-C <sub>3</sub> H <sub>7</sub>	-C <sub>3</sub> H <sub>7</sub>	-OCH <sub>3</sub>	591
130	-HNCOCCH <sub>3</sub>	-C <sub>3</sub> H <sub>7</sub>	-CH(CH <sub>3</sub> ) <sub>2</sub>	-OCH <sub>3</sub>	590
131	-HNCOCCH <sub>3</sub>	-CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub>	-H	-OCH <sub>3</sub>	565
132	-HNCOCCH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>3</sub> H <sub>7</sub> (4-SO <sub>2</sub> F phenyl)	-OCH <sub>3</sub>	585
133	-HNCOCCH <sub>3</sub>	-C <sub>3</sub> H <sub>7</sub> (4-SO <sub>2</sub> F phenyl)	-C <sub>3</sub> H <sub>7</sub> (4-SO <sub>2</sub> F phenyl)	-OCH <sub>3</sub>	580
134	-HNCOC(CH <sub>3</sub> ) <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	-H	-OCH <sub>3</sub>	566
135	-HNCOCCH <sub>3</sub>	-C <sub>2</sub> H <sub>4</sub> COOC <sub>3</sub> H <sub>7</sub>	-C <sub>2</sub> H <sub>4</sub> COOC <sub>3</sub> H <sub>7</sub>	-H	524
136	-HNCOCCH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>4</sub> H <sub>8</sub> COOC(CH <sub>3</sub> ) <sub>3</sub>	-OCH <sub>3</sub>	591
137	-HNCOCCH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> (phenyl)	-OCH <sub>3</sub>	588
138	-HNSO <sub>2</sub> phenyl	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-OCH <sub>3</sub>	573

Example 139i) Preparation of 2-nitro-4-fluorosulphonyl-6-chloroaniline.

2-Nitro-4-fluorosulphonylaniline (10g) was dispersed in 30% HCl (63.6g), cooled to 0-5°C and sodium chlorate (2g) dissolved in water (3.6g) added dropwise ensuring maintaining the temperature at 0-5°C. After 30 minutes reaction mixture drowned onto ice and precipitate collected, washed with water and suction dried to yield 8.5g of 2-Nitro-4-fluorosulphonyl-6-chloroaniline.

ii) 2-Nitro-4-fluorosulphonyl-6-chloroaniline (7.86mmol) was dispersed in a mixture of acetic:propionic acid (86:14; 25cm<sup>3</sup>), cooled to 0-5°C and nitrosyl sulphuric acid (7.86 mmol) added portionwise at 0-5°C. The reaction mixture was stirred for 10 minutes at 0-5°C then added dropwise to a mixture of the 3-(N,N-diethylamino) acetanilide (7.86 mmol), methanol (50cm<sup>3</sup>) and ice (50g). The resultant precipitate was filtered washed with water and then methanol and oven dried at 50°C. The dry dye has a  $\lambda_{\max}$  of 550nm and gives good fastness to washing, light and heat.

The following examples of dyes of Formula:



were prepared by the procedure of Example 139:

Example	R <sup>4</sup>	R <sup>1</sup>	R <sup>2</sup>	R <sup>5</sup>	$\lambda_{\text{max}}$ (nm)
140	-NHCOCH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-H	550
141	-NHCOCH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-OCH <sub>3</sub>	606
142	-CH <sub>3</sub>	-C <sub>4</sub> H <sub>9</sub> OCOCH <sub>3</sub>	-C <sub>4</sub> H <sub>9</sub> OCOCH <sub>3</sub>	-H	545
143	-CH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-H	535
144	-NHCOCH <sub>3</sub>	-C <sub>4</sub> H <sub>9</sub>	-C <sub>4</sub> H <sub>9</sub>	-OCH <sub>3</sub>	604
145	-HNCOCCH <sub>3</sub>	-C <sub>3</sub> H <sub>7</sub>	-C <sub>3</sub> H <sub>7</sub>	-OCH <sub>3</sub>	610
146	-HNCOC(CH <sub>3</sub> ) <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub> COOCH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub> COOCH <sub>3</sub>	-OCH <sub>3</sub>	545
147	-HNSO <sub>2</sub> CH <sub>3</sub>	-C <sub>3</sub> H <sub>7</sub>	-C <sub>3</sub> H <sub>7</sub>	-OCH <sub>3</sub>	588
148	-HNCOCCH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>3</sub> H <sub>7</sub>	-CH <sub>3</sub>	565
149	-HNCOCCH <sub>3</sub>	-CH(CH <sub>3</sub> ) <sub>2</sub>	-C <sub>3</sub> H <sub>7</sub>	-OCH <sub>3</sub>	602
150	-HNCOCCH(CH <sub>3</sub> ) <sub>2</sub>	-C <sub>3</sub> H <sub>7</sub>	-C <sub>3</sub> H <sub>7</sub>	-OCH <sub>3</sub>	608
151	-HNCOCCH <sub>3</sub>	-C <sub>4</sub> H <sub>9</sub>	-C <sub>2</sub> H <sub>5</sub> COOC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	-OCH <sub>3</sub>	603
152	-HNCOCCH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-OCH <sub>3</sub>	601.5
153	-HNCOC(CH <sub>3</sub> ) <sub>3</sub>	-H	-C <sub>2</sub> H <sub>5</sub> COOC <sub>3</sub> H <sub>7</sub>	-OCH <sub>3</sub>	565
154	-HNCOC(CH <sub>3</sub> ) <sub>3</sub>	-C <sub>2</sub> H <sub>4</sub> COOC <sub>3</sub> H <sub>7</sub>	-C <sub>2</sub> H <sub>4</sub> COOC <sub>3</sub> H <sub>7</sub>	-OCH <sub>3</sub>	574
155	-HNCOCCH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> (phenyl)	-OCH <sub>3</sub>	607

Example 156Preparation of 4-(5-chloro-4-fluorosulphonyl-2-nitrophenylazo)-3-acetamido-6-methoxy-N,N-dibutylaniline

i) 2-Nitro-5-chloroacetanilide (10g) was added cautiously to chlorosulphonic acid (40cm<sup>3</sup>) then heated at 120°C for 2 hours. The reaction mix was cooled to 50°C and drowned onto ice. The precipitate was filtered, washed with a little water and suction dried. This solid was dispersed in water (20 cm<sup>3</sup>), p-dioxane (20 cm<sup>3</sup>) and KF (10g). After refluxing for 2 hours the reaction mix was drowned into water, the precipitate filtered and suction dried. This solid was refluxed in water (50 cm<sup>3</sup>) and 36% HCl (50 cm<sup>3</sup>) for 1 hour, drowned onto ice and the precipitate collected. Yield 3.5g.

ii) 2-Nitro-4-fluorosulphonyl-5-chloroaniline (7.86 mmol) was dispersed in a mixture of acetic:propionic acid (86:14; 25cm<sup>3</sup>), cooled to 0-5°C and nitrosyl sulphuric acid (7.86 mmol) added portionwise at 0-5°C. The reaction mixture was stirred for 10 minutes at 0-5°C then added dropwise to a mixture of the 3-(N,N-dibutylamino)-4-methoxyacetanilide (7.86 mmol), methanol (50cm<sup>3</sup>) and ice (50g). The resultant precipitate was filtered washed with water and then methanol and oven dried at 50°C. The dry dye has a  $\lambda_{\text{max}}$  of 604nm and gives good

fastness to washing, light and heat.

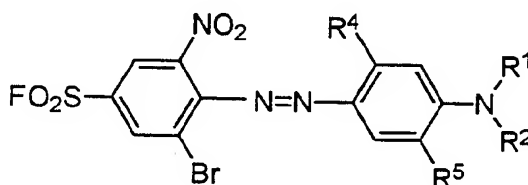
Example 157

Preparation of 4-(2-nitro-4-fluorosulphonyl-6-bromophenylazo)-3-acetamido-N,N-diethylaniline

i) 2-Nitro-4-fluorosulphonylaniline (5g) was dissolved in glacial acetic acid (50 cm<sup>3</sup>) and bromine (4.4g) added. Reaction mix warmed to 75°C for 2 hours then drowned onto ice, filtered, washed with water and suction dried. Yield 6.5g of yellow solid.

ii) 2-Nitro-4-fluorosulphonyl-6-bromoaniline (0.01 mol) was dispersed in a mixture of acetic:propionic acid (86:14; 25cm<sup>3</sup>), cooled to 0-5°C and nitrosyl sulphuric acid (0.01 mol) added portionwise at 0-5°C. The reaction mixture was stirred for 10 minutes at 0-5°C then added dropwise to a mixture of the 3-(N,N-diethylamino) acetanilide (0.01 mol), methanol (50cm<sup>3</sup>) and ice (50g). The resultant precipitate was filtered washed with water and then methanol and oven dried at 50°C. The dry dye has a  $\lambda_{\max}$  of 550nm and gives good fastness to washing, light and heat.

The following dyes of Formula:



were prepared by the procedure of Example 157:

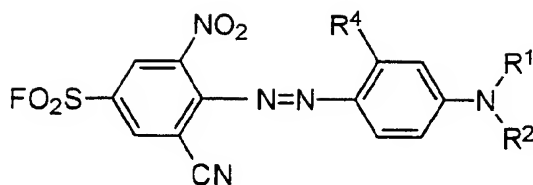
Example	R <sup>4</sup>	R <sup>1</sup>	R <sup>2</sup>	R <sup>5</sup>	$\lambda_{\max}$
158	-NHCOCH <sub>3</sub>	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-H	530
159	-NHCOCH <sub>3</sub>	-C <sub>4</sub> H <sub>9</sub>	-CH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub>	-H	556
160	-NHCOCH <sub>3</sub>	-C <sub>4</sub> H <sub>9</sub>	-C <sub>4</sub> H <sub>9</sub>	-H	555

Example 162

Preparation of 4-(2-nitro-4-fluorosulphonyl-6-cyanophenylazo)-3-acetamido-N,N-diethylaniline

Dye Example 157 (2.0g) was stirred at 90°C with CuCN (0.42g) and DMF (20cm<sup>3</sup>) for 3 hours. The reaction mix was drowned onto ice (50g) and the precipitate collected, washed with water and suction dried. The filter cake was slurried in dichloromethane, filtered and the filtrate evaporated to give a solid dye ( $\lambda_{\max}$  603nm) which gives good fastness to heat, washing and light.

The following dyes of Formula:



were prepared by the procedure of Example 162:

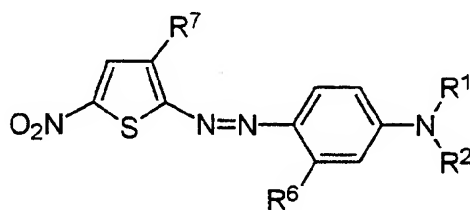
Example	R <sup>4</sup>	R <sup>1</sup>	R <sup>2</sup>	$\lambda_{\max}$ (nm)
163	-NHCOCH <sub>3</sub>	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	585
164	-NHCOCH <sub>3</sub>	-C <sub>4</sub> H <sub>9</sub>	-CH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub>	607
165	-NHCOCH <sub>3</sub>	-C <sub>4</sub> H <sub>9</sub>	-C <sub>4</sub> H <sub>9</sub>	606

#### Example 166

Preparation of 4-(3-carboethoxy-5-nitrothien-2-ylazo)-3-methyl-N-ethyl-N-(3-fluorosulphonylbenzoyloxy)ethyl aniline

4-(3-carboethoxy-5-nitrothienyl-2-ylazo)-3-methyl-N-ethyl-N-hydroxyethyl aniline (5mmol) was dissolved in chloroform (20cm<sup>3</sup>), potassium carbonate (0.7g) and 3-fluorosulphonylbenzoylchloride (1.2g) were added and the mixture refluxed for 2 hours. The reaction mixture was filtered and the filtrate evaporated to leave the solid dye,  $\lambda_{\max}$  = 588nm.

The following examples of dyes of Formula:



were prepared by the procedure of Example 166:

Example	R <sup>1</sup>	R <sup>2</sup>	R <sup>6</sup>	R <sup>7</sup>	$\lambda_{\text{max}}$ /nm
167	-C <sub>2</sub> H <sub>5</sub>	-C <sub>4</sub> H <sub>8</sub> OCO(3-SO <sub>2</sub> Fphenyl)	-CH <sub>3</sub>	-COOC <sub>2</sub> H <sub>5</sub>	616
168	-C <sub>2</sub> H <sub>4</sub> CN	-C <sub>2</sub> H <sub>4</sub> OCO(3-SO <sub>2</sub> Fphenyl)	-H	-NO <sub>2</sub>	575
169	-C <sub>2</sub> H <sub>4</sub> CN	-C <sub>2</sub> H <sub>4</sub> OCO(3-SO <sub>2</sub> Fphenyl)	-CH <sub>3</sub>	-NO <sub>2</sub>	594
170	-C <sub>2</sub> H <sub>4</sub> CN	-C <sub>2</sub> H <sub>4</sub> OCO(3-SO <sub>2</sub> Fphenyl)	-H	-COOC <sub>2</sub> H <sub>5</sub>	575
171	-C <sub>2</sub> H <sub>4</sub> CN	-C <sub>2</sub> H <sub>4</sub> OCO(3-SO <sub>2</sub> Fphenyl)	-H	-COCH <sub>3</sub>	563

#### Example 172

#### Preparation of 4-(3-carboethoxy-5-nitrothien-2-ylazo)-3-methyl-N-ethyl-N-(4-fluorosulphonylphenyl)methyl aniline

2-Amino-3-carboethoxy-5-nitrothiophene (0.01 mol) was dispersed in a mixture of acetic:propionic acid (86:14, 25cm<sup>3</sup>), cooled to 0-5°C and nitrosylsulphuric acid (0.01 mol) added portionwise at 0-5°C. The reaction mixture was stirred for 10 minutes at 0-5°C then added dropwise to a mixture of the N-ethyl-N-(4-fluorosulphonylbenzyl)-3-toluidine (0.01 mol), methanol (50cm<sup>3</sup>) and ice (50g). The resultant precipitate was filtered washed with water and then methanol and oven dried at 50°C. The dry dye has a  $\lambda_{\text{max}}$  of 580nm and gives good fastness to washing, light and heat.

The N-ethyl-N-(4-fluorosulphonylbenzyl)-3-toluidine was prepared as follows:

N-Ethyl-3-toluidine (0.01mol), potassium carbonate (0.01mol), DMF (50cm<sup>3</sup>) and 4-fluorosulphonylbenzyl bromide (0.2mol) were stirred at 100°C for 24 hours. The reaction mix was filtered, drowned onto ice and extracted with dichloromethane to give an impure product (22g). No further purification was required.

The 4-fluorosulphonylbenzylbromide was prepared as follows: Tosyl chloride (50g), bromine (43g) and carbon tetrachloride (500mls) were stirred at reflux while shining a UV lamp (365nm) onto the reaction. Once the solution became colourless the reaction was stopped and the solvent removed by evaporation. The resultant oil was refluxed in water (200mls) and potassium fluoride (47g) for three hours. After three hours the reaction mix was drowned onto ice (500g) and the precipitate collected, washed with water and dried in vacuo. Yield 34g of pale yellow crystals which by GLC is 54% required material, 17% starting material and 12% dibrominated species.

Example 173Preparation of 4-(3-carboethoxy-5-nitrothien-2-ylazo)-N-ethyl-N-(4-fluorosulphonylphenyl) methylaniline

2-Amino-3-carboethoxy-5-nitrothiophene (0.01mol) was dispersed in a mixture of acetic:propionic acid (86:14; 25cm<sup>3</sup>), cooled to 0-5°C and nitrosyl sulphuric acid (0.01 mol) added portionwise at 0-5°C. The reaction mixture was stirred for 10 minutes at 0-5°C then added dropwise to a mixture of the N-(4-fluorosulphonylbenzyl)-N-ethylaniline (0.01 mol), methanol (50cm<sup>3</sup>) and ice (50g). The resultant precipitate was filtered washed with water and then methanol and oven dried at 50°C. The dry dye has a  $\lambda_{\text{max}}$  of 560nm and gives good fastness to washing, light and heat.

The N-ethyl-N-(4-fluorosulphonylbenzyl)aniline was prepared as follows:

N-Ethylaniline (0.01mol), potassium carbonate (0.01mol), DMF (50cm<sup>3</sup>) and 4-fluorosulphonylbenzyl bromide (0.2mol) were stirred at 100°C for 24 hours. The reaction mix was filtered, drowned onto ice and extracted with dichloromethane to give an impure product (20g). No further purification was required.

Example 174Preparation of 4-(3-carboethoxy-5-nitrothien-2-ylazo)-N-ethyl-N-(4-fluorosulphonylphenyl) propylaniline

2-Amino-3-carboethoxy-5-nitrothiophene (0.01mol) was dispersed in a mixture of acetic:propionic acid (86:14; 25cm<sup>3</sup>), cooled to 0-5°C and nitrosyl sulphuric acid (0.01mol) added portionwise at 0-5°C. The reaction mixture was stirred for 10 minutes at 0-5°C then added dropwise to a mixture of the N-(4-fluorosulphonylphenylpropyl)-N-ethylaniline (0.01mol), methanol (50cm<sup>3</sup>) and ice (50g). The resultant precipitate was filtered washed with water and then methanol and oven dried at 50°C. The dry dye has a  $\lambda_{\text{max}}$  of 593nm and gives good fastness to washing, light and heat.

The N-ethyl-N-(4-fluorosulphonylphenylpropyl)aniline was prepared as follows:

N-Ethylaniline (0.01mol), potassium carbonate (0.01mol), DMF (50cm<sup>3</sup>) and 4-fluorosulphonylphenylpropyl bromide (0.2mol) were stirred at 100°C for 24 hours. The reaction mix was filtered, drowned onto ice and extracted with dichloromethane to give an impure product (25g). No further purification was required.

The 4-fluorosulphonylphenylpropylbromide was prepared as follows:

Phenylpropyl bromide (19.9g) was dissolved in chloroform (500mls) and chlorosulphonic acid (116g) added dropwise. Stirred for 12 hours at 40°C then drowned onto ice (10kg). The white precipitate was collected, redissolved in dichloromethane, washed with water, dried over magnesium sulphate and evaporated to a pale yellow oil that crystallised on standing. Yield 15g. This solid was dissolved in p-dioxane (50mls) and



KF (10g) and refluxed for three hours. After cooling to ambient the reaction mixture was drowned onto ice (400g), extracted with dichloromethane (3x200mls), dried over magnesium sulphate and evaporated to a brown oil. Yield 9g.

#### Example 175

##### Preparation of 4-(3-carboethoxy-5-nitrothien-2-ylazo)-N-(2-cyanoethyl)-N-(4-fluorosulphonylphenyl) ethylaniline

2-Amino-3-carboethoxy-5-nitrothiophene (0.01mol) was dispersed in a mixture of acetic:propionic acid (86:14; 25cm<sup>3</sup>), cooled to 0-5°C and nitrosyl sulphuric acid (0.01mol) added portionwise at 0-5°C. The reaction mixture was stirred for 10 minutes at 0-5°C then added dropwise to a mixture of the N-(2-cyanoethyl)-N-(4-fluorosulphonylphenylethyl)aniline (0.01mol), methanol (50cm<sup>3</sup>) and ice (50g). The resultant precipitate was filtered washed with water and then methanol and oven dried at 50°C. The dry dye has a  $\lambda_{\text{max}}$  of 547nm and gives good fastness to washing, light and heat.

The N-(2-cyanoethyl)-N-(4-fluorosulphonylphenylethyl)aniline was prepared as follows:

N-(2-cyanoethyl)aniline (0.01mol), potassium carbonate (0.01mol), DMF (50cm<sup>3</sup>) and 4-fluorosulphonylphenylethylbromide (0.01mol) were stirred at 100°C for 24 hours. The reaction mix was filtered, drowned onto ice and extracted with dichloromethane to give an impure product (25g). No further purification was required.

The 4-fluorosulphonylphenylethylbromide was prepared as follows:

Phenylethyl bromide (36.5g) was dissolved in chloroform (500mls) and chlorosulphonic acid (233g) added dropwise. Stirred for 12 hours at ambient then drowned onto ice (10kg). The white precipitate was collected, redissolved in dichloromethane, washed with water, dried over magnesium sulphate and evaporated to a pale yellow oil that crystallised on standing. Yield 40.8g. This solid was dissolved in p-dioxane (200mls) and KF (24.7g) and refluxed for three hours. After cooling to ambient the reaction mixture was drowned onto ice (700g), extracted with dichloromethane (3x200mls), dried over magnesium sulphate and evaporated to a brown oil. Yield 33.7g.

#### Example 176

##### Preparation of 4-(3,5-dinitrothien-2-ylazo)-N-ethyl-N-(4-fluorosulphonylphenyl) methyl aniline

2-Amino-3,5-dinitrothiophene (0.01mol) was dispersed in a mixture of acetic:propionic acid (86:14; 25cm<sup>3</sup>), cooled to 0-5°C and nitrosyl sulphuric acid (0.01mol) added portionwise at 0-5°C. The reaction mixture was stirred for 10 minutes at 0-5°C then added dropwise to a mixture of the N-ethyl-N-(4-fluorosulphonylbenzyl)aniline (0.01mol), methanol (50cm<sup>3</sup>) and ice (50g). The resultant precipitate

was filtered washed with water and then methanol and oven dried at 50°C. The dry dye has a  $\lambda_{\text{max}}$  of 605nm and gives good fastness to washing, light and heat.

Example 177

Preparation of 4-(3,5-dinitrothien-2-ylazo)-N-ethyl-N-(4-fluorosulphonylphenyl) propyl aniline

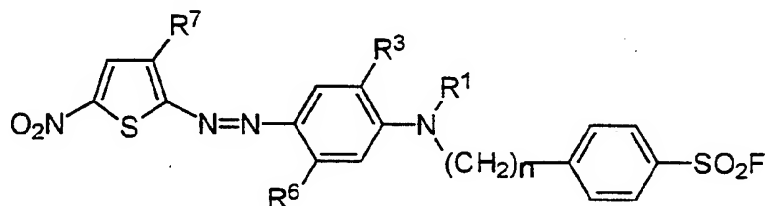
2-Amino-3,5-dinitrothiophene (0.01mol) was dispersed in a mixture of acetic:propionic acid (86:14; 25cm<sup>3</sup>), cooled to 0-5°C and nitrosyl sulphuric acid (0.01 mol) added portionwise at 0-5°C. The reaction mixture was stirred for 10 minutes at 0-5°C then added dropwise to a mixture of the N-ethyl-N-(4-fluorosulphonylphenylpropyl) aniline (0.01 mol), methanol (50cm<sup>3</sup>) and ice (50g). The resultant precipitate was filtered washed with water and then methanol and oven dried at 50°C. The dry dye has a  $\lambda_{\text{max}}$  of 617nm and gives good fastness to washing, light and heat.

Example 178

Preparation of 4-(3,5-dinitrothien-2-ylazo-N-(2-cyanoethyl)-N-(4-fluorosulphonylphenyl) ethyl aniline

2-Amino-3,5-dinitrothiophene (0.01mol) was dispersed in a mixture of acetic:propionic acid (86:14; 25cm<sup>3</sup>), cooled to 0-5°C and nitrosyl sulphuric acid (0.01 mol) added portionwise at 0-5°C. The reaction mixture was stirred for 10 minutes at 0-5°C then added dropwise to a mixture of the N-(2-cyanoethyl), N-(4-fluorosulphonylphenylethyl) aniline (0.01mol), methanol (50cm<sup>3</sup>) and ice (50g). The resultant precipitate was filtered, washed with water and methanol and oven dried at 50°C. The dry dye has a  $\lambda_{\text{max}}$  of 580nm and gives good fastness to washing, light and heat.

The following examples of dyes of Formula:



were prepared using the procedure of Example 172, the fluorosulphonylphenylalkyl bromides were prepared as described in examples 172, 174 and 175 as appropriate.

EG	R <sub>7</sub>	R <sub>6</sub>	R <sub>3</sub>	R <sub>1</sub>	n	λ <sub>max</sub> / nm
179	-COOC <sub>2</sub> H <sub>5</sub>	-H	-H	-C <sub>2</sub> H <sub>5</sub>	3	593
180	-COOC <sub>2</sub> H <sub>5</sub>	-NHCOCH <sub>3</sub>	-H	-C <sub>2</sub> H <sub>5</sub>	3	605.5
181	-COOC <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-H	-CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub>	3	614
182	-COOC <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-OCH <sub>3</sub>	-C <sub>4</sub> H <sub>9</sub>	3	636
183	-COOC <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-OCH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	3	631
184	-COOC <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-OCH <sub>3</sub>	-CH(CH <sub>3</sub> ) <sub>2</sub>	1	594
185	-COOC <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-OCH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	2	621.5
186	-COOC <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	-OCH <sub>3</sub>	-H	2	595
187	-COOC <sub>2</sub> H <sub>5</sub>	-NHCOCH <sub>3</sub>	-OCH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	1	641
188	-COOC <sub>2</sub> H <sub>5</sub>	-H	-H	-C <sub>4</sub> H <sub>9</sub>	3	585
189	-NO <sub>2</sub>	-H	-H	-C <sub>4</sub> H <sub>9</sub>	3	637

Example 190Preparation of 4-(2,4-dinitrophenylazo)-3-acetamido-6-methoxy-N-secbutyl-N-(4-fluorosulphonylphenyl)methyl aniline

2,4-Dinitroaniline (0.01mol) was dispersed in a mixture of acetic:propionic acid (86:14; 25cm<sup>3</sup>), cooled to 0-5°C and nitrosyl sulphuric acid (0.01mol) added portionwise at 0-5°C. The reaction mixture was stirred for 10 minutes at 0-5°C then added dropwise to a mixture of the 3-(N-(4-fluorosulphonylbenzyl)-N-sec butylamino)-4-methoxyacetanilide (0.01mol), methanol (50cm<sup>3</sup>) and ice (50g). The resultant precipitate was filtered washed with water and then methanol and oven dried at 50°C. The dry dye has a λ<sub>max</sub> of 575nm and gives good fastness to washing, light and heat.

The 3-(N-(4-fluorosulphonylbenzyl)-N-sec-butylamino)-4-methoxyacetanilide was prepared as follows:  
3-(N-sec-butyl)amino-4-methoxyacetanilide, potassium carbonate (0.01mol), DMF (50cm<sup>3</sup>) and 4-fluorosulphonylbenzyl bromide (0.2mol) were stirred at 100°C for 24 hours. The reaction mix was filtered, drowned onto ice and extracted with dichloromethane to give an impure product (22g). No further purification was required.

Example 191Preparation of 4-(2,4-dinitro-6-bromophenylazo)-3-acetamido-6-methoxy-N-secbutyl-N-(4-fluorosulphonylphenyl)methyl aniline

2,4-Dinitro-6-bromoaniline (0.01mol) was dispersed in a mixture of acetic:propionic acid (86:14; 25cm<sup>3</sup>), cooled to 0-5°C and

nitrosyl sulphuric acid (0.01mol) added portionwise at 0-5°C. The reaction mixture was stirred for 10 minutes at 0-5°C then added dropwise to a mixture of the 3-(N-(4-fluorosulphonylbenzyl)-N-sec butylamino)-4-methoxyacetanilide (0.01mol), methanol (50cm<sup>3</sup>) and ice (50g). The resultant precipitate was filtered washed with water and then methanol and oven dried at 50°C. The dry dye has a  $\lambda_{\max}$  of 594nm and gives good fastness to washing, light and heat.

Example 192

Preparation of 4-(2,4-dinitro-6-cyanophenylazo)-3-acetamido-6-methoxy-N-secbutyl-N-(4-fluorosulphonylphenyl)methyl aniline

The dye from Example 191 (2.2mmol) was dissolved in DMF (30cm<sup>3</sup>) and CuCN (0.2g) and stirred at 60°C for 1 hour. The reaction mix was drowned onto ice and the precipitate filtered. The dried filter cake was slurried in dichloromethane, filtered and the filtrate evaporated to a solid dye with  $\lambda_{\max}$  of 642nm.

Example 193

Preparation of 4-(2,4-dinitro-6-chlorophenylazo)-3-methyl-6-methoxy-N-n-butyl-N-(4-fluorosulphonylphenyl)n-propyl aniline

The method of Example 191 was used except that 2,4-dinitro-6-chloroaniline (0.01 mol) was used in place of the 2,4-dinitro-6-bromoaniline and 3-(N-(4-fluorosulphonylphenyl)propyl-N-n-butyl-6-methoxy)toluidine (0.01 mol) was used in place of the 3-(N-(4-fluorosulphonylbenzyl)-N-secbutyl-4-methoxyacetanilide. The dye has a  $\lambda_{\max}$  of 586.5nm and gives good fastness to washing, light and heat.

Example 194

Preparation of 4-(2,4-dinitrophenylazo)-3-methyl-N-ethyl-N-(4-(3-fluorosulphonylbenzoyloxy)n-butyl) aniline

2,4-Dinitroaniline (0.01mol) was dispersed in a mixture of acetic: propionic acid (86:14; 25cm<sup>3</sup>), cooled to 0-5°C and nitrosyl sulphuric acid (0.01mol) added portionwise at 0-5°C. The reaction mixture was stirred for 10 minutes at 0-5°C then added dropwise to a mixture of the N-ethyl-N-hydroxybutyl-3-toluidine (0.01mol), methanol (50cm<sup>3</sup>) and ice (50g). The resultant precipitate was filtered washed with water and then methanol and oven dried at 50°C. The hydroxy dye (5 mmol) was dissolved in chloroform (20 cm<sup>3</sup>), potassium carbonate (0.7g) and m-(sulphonylfluoride) benzoyl chloride (1.2g) and refluxed for 2 hours. The reaction mix was filtered and the filtrate evaporated to yield a solid violet dye which gives good fastness to washing, light and heat.

Example 195

Preparation of 4-(2,4-dinitro-6-bromophenylazo)-3-acetamido-N-n-propyl-N-(3-fluorosulphonylbenzoyloxy)ethyl aniline

2,4-Dinitro-6-bromoaniline (0.01mol) was dispersed in a

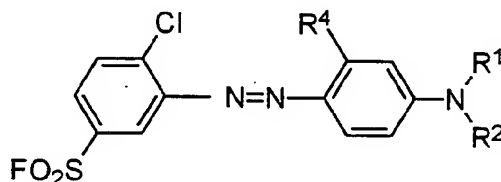
mixture of acetic:propionic acid (86:14; 25cm<sup>3</sup>), cooled to 0-5°C and nitrosyl sulphuric acid (0.01mol) added portionwise at 0-5°C. The reaction mixture was stirred for 10 minutes at 0-5°C then added dropwise to a mixture of the 3-(N-propyl-N-hydroxyethyl) acetanilide (0.01mol), methanol (50cm<sup>3</sup>) and ice (50g). The resultant precipitate was filtered washed with water and then methanol and oven dried at 50°C. The hydroxy dye (5mmol) was dissolved in chloroform (20cm<sup>3</sup>), potassium carbonate (0.7g) and m-(sulphonylfluoride) benzoyl chloride (1.2g) and refluxed for 2 hours. The reaction mix was filtered and the filtrate evaporated to yield a solid dye ( $\lambda_{\max}$  552nm) which gives good fastness to washing, light and heat.

Example 196

Preparation of 4-(2-chloro-5-fluorosulphonylphenylazo)-N-ethyl-N-benzyl aniline

3-Amino-4-chloro benzene sulphonyl fluoride (2 parts) was stirred in acetic/propionic acid 86/14 vol/vol (25 parts) and cooled to 0-5°C. Nitrosyl sulphuric acid solution (3.8 parts) was added dropwise at 0-5°C and stirred under these conditions for 2 hours. The diazo solution was then added to a mixture of N-ethyl-N-benzyl aniline (2.7 parts), methanol (100 parts) and sulphamic acid (1 part) stirring at 0-5°C. After stirring under these conditions for 30 mins, ice/water (100 parts) was added and the mixture stirred for a further 1 hour. The product was isolated by filtration, washed with water and pulled dry. The damp solid was then slurried in methanol (100 parts) and re-filtered. Dried at 50°C to yield 4-(2-chloro-5-fluorosulphonyl phenyl azo)-N-ethyl-N-benzyl aniline (2.3 parts).

When applied to polyester materials from an aqueous dispersion, the dye gave yellow shades.  $\lambda_{\max}$  463nm. The following examples of dyes of Formula:



were prepared by the procedure of Example 196:

Example	R <sup>1</sup>	R <sup>2</sup>	R <sup>4</sup>	$\lambda_{\max}/\text{nm}$
197	-C <sub>2</sub> H <sub>4</sub> CN	-C <sub>2</sub> H <sub>4</sub> CN	-H	421
198	-C <sub>2</sub> H <sub>4</sub> CN	-C <sub>2</sub> H <sub>4</sub> COOCH <sub>2</sub> CN	-H	429
199	-C <sub>2</sub> H <sub>4</sub> CN	-C <sub>2</sub> H <sub>4</sub> CN	-CH <sub>3</sub>	429
200	-C <sub>2</sub> H <sub>4</sub> CN	-C <sub>2</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>5</sub>	-NHCOCH <sub>3</sub>	466
201	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-NHCOCH <sub>3</sub>	473
202	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> CN	-H	442
203	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> CN	-CH <sub>3</sub>	449
204	-C <sub>4</sub> H <sub>9</sub>	-C <sub>2</sub> H <sub>4</sub> CN	-H	444
205	-C <sub>4</sub> H <sub>9</sub> OCOCH <sub>3</sub>	-C <sub>4</sub> H <sub>9</sub> OCOCH <sub>3</sub>	-CH <sub>3</sub>	477
206	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> phenyl	-CH <sub>3</sub>	469

Example 207Preparation of 4-(2-chloro-4-fluorosulphonylphenylazo)-N-ethyl-N-benzyl aniline

3-Chloro-4-amino benzene sulphonylfluoride (1 part) was stirred in acetic/propionic acid 86/14 vol/vol (15 parts) and cooled to 0-5°C. Nitrosyl sulphuric acid solution (1.9 parts) was added dropwise then stirred at 0-5°C for 2 hours. The diazo solution was then added to a stirred mixture of N-ethyl-N-benzyl aniline (2.0 parts), methanol (50 parts), sulphamic acid (0.5 parts) and sodium acetate (5 parts) with ice/water (100 parts) at 0-5°C. After stirring under these conditions for 1 hour, the dye was filtered off and washed well with water. The damp solid was slurried in methanol (100 parts) and re-filtered. Dried at 50°C to yield the product 4-(2-chloro-4-fluorosulphonyl phenylazo)-N-ethyl-N-benzyl aniline (1.5 parts). When applied to polyester materials from an aqueous dispersion the dye gave orange shades.  $\lambda_{\max}$  483nm

Example 208Preparation of 4-(2-chloro-4-fluorosulphonylphenylazo)-3-acetamido-N,N-bis(2-acetoxyethyl) aniline

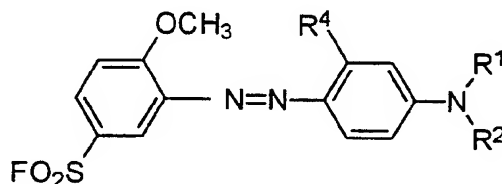
The procedure of Example 207 was repeated except that in place of 2 parts of N-ethyl-N-benzyl aniline; 2 parts of N,N-bis(2-acetoxyethyl) aminoacetanilide were used to yield the product, 4-(2-chloro-4-fluorosulphonyl phenylazo)-3-acetamido-N,N-bis(2-acetoxyethyl) aniline (1.2 parts). When applied to polyester materials from an aqueous dispersion, the dye gave orange shades.  $\lambda_{\max}$  494nm.

Example 209Preparation of 4-(2-methoxy-5-fluorosulphonylphenylazo)-3-methyl-N-ethyl-N-benzyl aniline

3-Amino-4-methoxy benzene sulphonylfluoride (1 part) was stirred in acetic/propionic acid 86/14 vol/vol (15 parts) and cooled to

0-5°C. Nitrosyl sulphuric acid solution (1.9 parts) was dropwise and stirred at 0-5°C for 2 hours. The diazo solution was then added to a stirred mixture of N-ethyl-N-benzyl-m-toluidine (1.3 parts), methanol (50 parts), sulphamic acid (0.5 parts) and sodium acetate (5 parts) stirring in ice/water at 0-5°C. After stirring for 2 hours under these conditions, the dye was filtered off and washed well with water. The damp solid was slurried in water and re-filtered. The dye was then stirred in methanol at room temperature for 1 hour, filtered, and dried at 50°C to yield the product, 4-(2-methoxy-5-fluorosulphonyl phenylazo)-3-methyl-N-ethyl-N-benzyl aniline (1.5 parts). When applied to polyester materials from an aqueous dispersion, the dye gave yellow shades.  $\lambda_{\text{max}}$  450.

The following examples of dyes of Formula:



were prepared by the procedure of Example 209:

Example	R <sup>1</sup>	R <sup>2</sup>	R <sup>4</sup>	$\lambda_{\text{max}}$ /nm
210	-C <sub>4</sub> H <sub>9</sub> OCOCH <sub>3</sub>	-C <sub>4</sub> H <sub>9</sub> OCOCH <sub>3</sub>	-CH <sub>3</sub>	455
211	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> CN	-H	449
212	-C <sub>2</sub> H <sub>5</sub>	-H	-CH <sub>3</sub>	429
213	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> phenyl	-H	444

#### Example 214

##### Preparation of 4-(4-chloro-5-fluorosulphonylphenylazo)-N,N-bis (2-cvanoethyl) aniline

i) 2-Chloro-5-nitro benzene sulphonic acid (484 parts) was charged to a flask then quickly added thionyl chloride (1190 parts) and dimethyl formamide (12 parts). The resultant slurry was heated to 60°C and stirred at 60-65°C for a total of 5 hours. The mixture was cooled to room temperature then poured onto ice/water. The precipitated solid was filtered off and washed with cold water before drying in vac oven to yield the product 2-chloro-5-nitro benzene sulphonylchloride (395 parts).

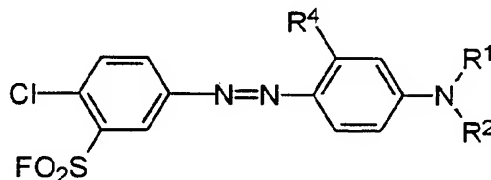
ii) 2-Chloro-5-nitro benzene sulphonylchloride (40 parts) was stirred in p-dioxane (48 parts) at room temperature. Potassium fluoride

(10 parts) dissolved in water (35 parts) was added, and the mixture heated to 70°C. Stirred at 70°C for 4 hours then cooled to room temperature and poured onto ice/water. Allowed to stand for 2 days then filtered off the precipitate and dried in air to yield the product 2-chloro-5-nitro benzene sulphonylfluoride (36 parts).

iii) The 2-chloro-5-nitro benzene sulphonylfluoride (2.4 parts) was stirred in glacial acetic acid (25 parts) with iron powder (2 parts). Heated to reflux and stirred at reflux for 2.5 hours, then cooled to room temperature, poured onto ice/water and allowed to stand at room temperature overnight. The resultant precipitate was filtered off and dried in air to yield the product 2-chloro-5-amino benzene sulphonylfluoride (0.8 parts).

iv) 2-Chloro-5-amino benzene sulphonylfluoride (2.1 parts) was stirred in acetic/propionic acid 86/14 vol/vol (25 parts) and cooled to 0-5°C. Nitrosyl sulphuric acid solution (3.8 parts) was added and stirred at 0-5°C for 3 hours. The diazo solution was then added to a mixture of N,N-bis(2-cyanoethyl) aniline (2.1 parts), methanol (75 parts) and sulphamic acid (1 part) stirring in ice/water (75 parts) at 0-5°C. Stirred under these conditions for 1 hour then allowed to stand at room temperature overnight before filtering off the dye. The solid was dried overnight to yield the product 4-(4-chloro-5-fluorosulphonyl phenylazo)-N,N-bis(2-cyanoethyl) aniline (3.6 parts). The dye, when applied to polyester material from an aqueous dispersion, gave yellow shades.  $\lambda_{\text{max}}$  414nm.

The following Examples of dyes of Formula:



were prepared by the procedure of Example 214:



Example	R <sup>1</sup>	R <sup>2</sup>	R <sup>4</sup>	$\lambda_{\text{max}}/\text{nm}$
215	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-C <sub>2</sub> H <sub>4</sub> OCOCH <sub>3</sub>	-NHCOCH <sub>3</sub>	476
216	-C <sub>2</sub> H <sub>4</sub> CN	-C <sub>2</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>5</sub>	-NHCOCH <sub>3</sub>	466
217	-C <sub>2</sub> H <sub>4</sub> CN	-C <sub>2</sub> H <sub>4</sub> CN	-CH <sub>3</sub>	421
218	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> phenyl	-H	459
219	-C <sub>2</sub> H <sub>4</sub> CN	-C <sub>2</sub> H <sub>4</sub> COOCH <sub>2</sub> CN	-H	421

Example 220Preparation of 4-(3-nitro-5-fluorosulphonylthien-2-ylazo)-3-acetamido-N,N-diethylamino) aniline

i) 2-Chlorosulphonyl-5-chlorothiophene (19.8 parts) was added to fuming nitric acid (80 parts), allowing to exotherm to 35°C. Heated to 50°C and stirred under these conditions for 2 hours. Cooled to room temperature then poured onto ice/water with vigorous stirring. The white solid was filtered off and dried to yield the product 2-chlorosulphonyl-4-nitro-5-chlorothiophene (19 parts).

ii) 2-Chlorosulphonyl-4-nitro-5-chlorothiophene (20.1 parts) were stirred in p-dioxane (80 parts) at room temperature. Potassium fluoride (5.2 parts) in water (20 parts) was added and the mixture heated to 50°C. Stirred under these conditions for 4 hours, then cooled and poured onto ice/water. Ethyl acetate was then added to extract the product and separated. Dried over magnesium sulphate then screened and concentrated to yield the product 2-fluorosulphonyl-4-nitro-5-chlorothiophene (20.4 parts).

iii) The 2-fluorosulphonyl-4-nitro-5-chlorothiophene (20.4 parts), was added to methanol (240 parts) with hexamine (22.5 parts). Heated to reflux and stirred under these conditions for 4 hours. Cooled to room temperature and poured onto 10% sulphuric acid solution (250 parts). The product was extracted out with ethyl acetate, separated and dried over magnesium sulphate, then screened and concentrated to yield the product 2-fluorosulphonyl-4-nitro-2-aminothiophene (16 parts).

iv) 2-Fluorosulphonyl-4-nitro-5-aminothiophene (4.2 parts) was added over 30 mins to a stirred solution of acetic/propionic acid 86/14 vol/vol (60 parts) with nitrosyl sulphuric acid solution (10 parts) at 0-5°C. Stirred under these conditions for 4 hours. The diazo solution was then added to a mixture of 3-N,N-diethyl aminoacetanilide (4.2 parts), water (40 parts), methanol (15 parts), and sulphamic acid (1 part) stirring in 50% sulphuric acid solution at 0-5°C. Stirred under these conditions for 45 mins then filtered off the dye and washed well

with water. Dried in the oven overnight to yield the product 4-(3-nitro-5-fluorosulphonylthien-2-ylazo)-3-acetamido-N,N-(diethylamino) aniline (0.6 parts). When applied to polyester materials from an aqueous dispersion, the dye gave blue shades.  $\lambda_{\text{max}}$  615nm.

Example 221

Preparation of 4-(3-nitro-5-fluorosulphonylthien-2-ylazo)-3-methyl-N,N-diethylaminoaniline

The procedure of Example 220iv) was repeated except that in place of the 3-N,N-diethylaminoacetanilide 0.4 parts of 3-methyl-N,N-diethylaminoaniline was used to yield 4-(3-nitro-5-fluorosulphonylthien-2-ylazo)-3-methyl-N,N-diethylaminoaniline (0.3 parts). When applied to polyester materials from an aqueous dispersion the dye gave blue shades.  $\lambda_{\text{max}}$  629nm.

**General Method for the Preparation of Dye Examples 222 - 238**

i) Preparation of 2-nitro-4-fluorosulphonylaniline

N-acetyl sulphanilyl chloride (100g) was dissolved in concentrated sulphuric acid (515 cm<sup>3</sup>), cooled to 4°C and a mixture of concentrated nitric acid (38.6 cm<sup>3</sup>) and concentrated sulphuric acid (42.9 cm<sup>3</sup>) added dropwise maintaining the temperature at 4-6°C. After 1 hour the reaction mix was drowned onto ice and the precipitate collected, extracted into dichloromethane and evaporated to a yellow solid (92g). 31g of this yellow solid was refluxed for 3 hours in water (20 cm<sup>3</sup>), p-dioxane (20 cm<sup>3</sup>) and KF (19.4g) then drowned onto ice and the precipitate collected. This precipitate was refluxed in absolute ethanol (35 cm<sup>3</sup>) and concentrated hydrochloric acid (35 cm<sup>3</sup>) for 1 hour then drowned onto ice, filtered and suction dried. Recrystallisation from ethanol yielded 8.7g of the required compound.

ii) Preparation of 2-nitro-4-fluorosulphonyl-6-chloroaniline

2-Nitro-5-chloroacetanilide (10g) was added cautiously to chlorosulphonic acid (40cm<sup>3</sup>) then heated at 120°C for 2 hours. The reaction mix was cooled to 50°C and drowned onto ice. The precipitate was filtered, washed with a little water and suction dried. This solid was dispersed in water (20cm<sup>3</sup>), p-dioxane (20cm<sup>3</sup>) and KF (10g). After refluxing for 2 hours the reaction mix was drowned into water, the precipitate filtered and suction dried. This solid was refluxed in water (50cm<sup>3</sup>) and 36% HCl (50cm<sup>3</sup>) for 1 hour, drowned onto ice and the precipitate collected. Yield 3.5g.

2-Nitro-4-fluorosulphonylaniline (0.01mol) (for dyes 222-230) or 2-nitro-6-chloro-4-fluorosulphonyl-aniline (0.01mol) (for dyes 231-238) was dispersed in a mixture of acetic:propionic acid (86:14) (25ml) and cooled to 0-5°C and nitrosylsulphuric acid (0.01mol) was then added

portionwise at 0-5°C. The reaction mixture was stirred for 10 min. at 0-5°C and then added dropwise to a mixture of the required coupler (0.01mol), methanol (50ml) and ice (50g) maintaining the acidity between pH3 and pH5 by addition of sodium acetate. The resultant precipitate was filtered, washed with water and then methanol 1:1 water and dried in air. The dry dye, when applied to polyester as an aqueous dispersion, gave good fastness to washing, light and heat.

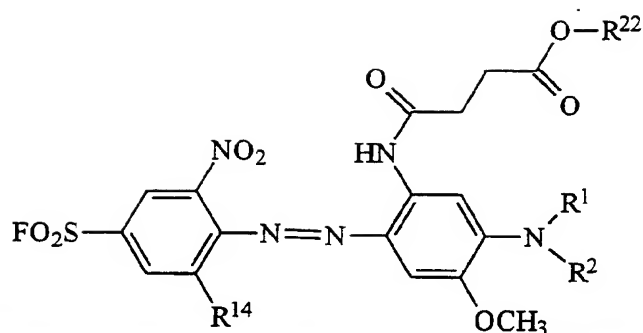
(i) Preparation of Couplers for Dye Examples 222 - 224, 226, 229 and 231 - 235 - Method 1:

Dye Examples 222 - 224, 226, 229 and 231 - 235 were prepared from the appropriate N,N-dialkyl-(3-ethylsuccinamido-6-methoxy)aniline coupling components which were prepared according to the following method. A mixture of 3-(N,N-dialkyl)-4-methoxyaniline (0.01mol), ethylsuccinyl chloride (0.01mol) and pyridine (0.01mol) in dichloromethane (50ml) was stirred and heated under gentle reflux for 4h and then allowed to cool and was then drowned out into water. The resulting product was extracted into dichloromethane, dried (MgSO<sub>4</sub>) and evaporated to dryness in vacuo to yield the required coupler as a brown oil.

(ii) Preparation of Couplers for Dye Examples 225, 227, 228, 230 and 236 - 238 - Method 2:

Dye Examples 225, 227, 228, 230 and 236 - 238 were prepared from the appropriate N,N-dialkyl-(3-ethylsuccinamido-6-methoxy)aniline coupling components which were prepared according to the following method. A mixture of 3-(N,N-dialkylamino)-4-methoxyaniline (0.01mol) and succinic anhydride (0.01mol) in anhydrous toluene (50ml) was stirred for 1.5h and then evaporated to dryness in vacuo to give a brown gum. The brown gum (the carboxylic acid intermediate) was esterified by treatment with an appropriate alcohol (0.1mol) and conc. sulphuric acid (1ml) at 100°C for 1h and was then allowed to cool. The mixture was drowned out into water and the product was extracted into ethyl acetate, dried (MgSO<sub>4</sub>) and evaporated to dryness in vacuo to yield the required coupler as a brown oil.

Dye Examples 222 - 238 are summarised below:-



Example	R <sup>14</sup>	R <sup>1</sup>	R <sup>2</sup>	R <sup>22</sup>	max/nm
222	-H	-C <sub>3</sub> H <sub>7</sub>	-C <sub>3</sub> H <sub>7</sub>	-C <sub>2</sub> H <sub>5</sub>	592
223	-H	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	590
224	-H	-C <sub>4</sub> H <sub>9</sub>	-C <sub>4</sub> H <sub>9</sub>	-C <sub>2</sub> H <sub>5</sub>	594
226	-H	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	591
226	-H	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> phenyl	-C <sub>2</sub> H <sub>5</sub>	585
227	-H	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-CH(CH <sub>3</sub> )CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	590
228	-H	C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> phenyl	591
229	-H	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>4</sub> phenyl	-C <sub>2</sub> H <sub>5</sub>	588
230	-H	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> (tetrahydrofuran-2-yl)	590
231	-Cl	-C <sub>3</sub> H <sub>7</sub>	-C <sub>3</sub> H <sub>7</sub>	-C <sub>2</sub> H <sub>5</sub>	609
232	-Cl	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> phenyl	-C <sub>2</sub> H <sub>5</sub>	601
233	-Cl	-C <sub>4</sub> H <sub>9</sub>	-C <sub>4</sub> H <sub>9</sub>	-C <sub>2</sub> H <sub>5</sub>	610
234	-Cl	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	607
235	-Cl	-C <sub>2</sub> H <sub>5</sub>	-CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	606
236	-Cl	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	607
237	-Cl	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-CH(CH <sub>3</sub> )CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	607
238	-Cl	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> phenyl	607

#### Preparation of Dye Examples 239 - 246

Dye Examples 239 - 246 were prepared using the same **general method** as was used for the preparation of dye examples 222 - 238. The dyes, when applied to polyester as aqueous dispersions, gave good fastness to washing light and heat.

The couplers for dye Examples 239, 240 and 246 were prepared from 3-(N,N-diethylamino)-4-methoxyaniline according to the method 1 using acetylsalicyl chloride (0.01mol) in place of ethylsuccinyl chloride.

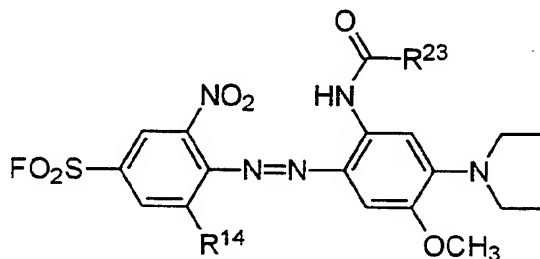
5 The coupler for dye Example 241 was prepared from 3-(N,N-diethylamino)-4-methoxyaniline according to the method 1 using butylchloroformate (0.01mol) in place of ethylsuccinyl chloride. The coupler for dye Example 242 was prepared from 3-(N,N-diethylamino)-4-methoxyaniline according to the method 1 using ethylmalonyl chloride  
10 (0.01mol) in place of ethylsuccinyl chloride.

The coupler for dye Example 243 was prepared from 3-(N,N-diethylamino)-4-methoxyaniline according to the method 2 using maleic anhydride (0.01mol) in place of succinic anhydride and ethanol as the esterifying alcohol.

15 The coupler for dye Example 244 was prepared from 3-(N,N-diethylamino)-4-methoxyaniline according to the method 2 using 2,2-dimethylsuccinic anhydride (0.01mol) in place of succinic anhydride and ethanol as the esterifying alcohol.

20 The coupler for dye Example 245 was prepared from 3-(N,N-diethylamino)-4-methoxyaniline according to the method 1 using 4-methoxycarbonylphenylchloroformate (0.01mol) in place of ethylsuccinyl chloride.

Dye Examples 239 - 246 are summarised below :-



Example	R <sup>14</sup>	R <sup>23</sup>	$\lambda_{\max}/\text{nm}$
239	-H	2-OCOCH <sub>3</sub> phenyl	598
240	-H	2-OHphenyl	590
241	-H	-OC <sub>4</sub> H <sub>9</sub>	587
242	-H	-CH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	591
243	-H	-CH=CHCOOC <sub>2</sub> H <sub>5</sub>	596
244	-H	-CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	592
245	-H	4-COOC <sub>2</sub> H <sub>5</sub> phenyl	573
246	-Cl	4-OCOCH <sub>3</sub> phenyl	601

Example 247Preparation of 5-(2,5-dichloro-4-fluorosulphonylphenylazo)-4,6-diaminopropylthiopyrimidine

The procedure of Example 1 was repeated except that in place of the 1.6 parts of N,N-bis-(2-cyanoethyl)aniline; 1.5 parts of 4,6-diamino-2-propylthiopyrimidine were used. The product, 5-(2,5-dichloro-4-fluorosulphonylphenylazo)-4,6-diaminopropylthiopyrimidine (3.4 parts)  $\lambda_{\max}=420\text{nm}$ , when applied to polyester materials from an aqueous dispersion gives bright yellow shades with excellent fastness to light and wet treatments.

Example 248Preparation of 4-(2,5-dichloro-4-fluorosulphonylphenylazo)-3-chloro-N-ethyl,N-methylphthalimidoaniline

The procedure of Example 1 was repeated except that in place of the 1.6 parts of N,N-bis-(2-cyanoethyl)aniline; 2.6 parts of 3-chloro-N-ethyl,N-methylphthalimidoaniline were used. The product, 4-(2,5-dichloro-4-fluorosulphonylphenylazo)-3-chloro-N-ethyl,N-methylphthalimidoaniline (4.0 parts)  $\lambda_{\max}=455\text{nm}$ , when applied to polyester materials from an aqueous dispersion gives orange shades with excellent fastness to light and wet treatments.

Example 249Preparation of 4-(2,5-dichloro-4-fluorosulphonylphenylazo)-3-methylmorpholinobenzene

The procedure of Example 1 was repeated except that in place of the 1.6 parts of N,N-bis-(2-cyanoethyl)aniline; 1.5 parts of 3-methylmorpholinobenzene were used. The product, 4-(2,5-dichloro-4-fluorosulphonylphenylazo)-3-methylmorpholinobenzene (1.9 parts)  $\lambda_{\max}=480\text{nm}$ , when applied to polyester materials from an aqueous dispersion gives dull bluish red shades with excellent fastness to light and wet treatments.

Example 250Preparation of 4-(2-nitro-4-fluorosulphonyl-6-chlorophenylazo)-1-(N-ethylamino)naphthalene

The procedure of Example 139 was used except that 1-(N-ethylamino) naphthalene (7.86 nmol) was used in place of the 3-(N,N-diethylamino) acetanilide. The dye has a  $\lambda_{\max}$  of 571 nm.

Example 251Preparation of 4-(2-nitro-4-fluorosulphonyl-6-chlorophenylazo)-1-(N-ethyl-N-n-propylamino)naphthalene

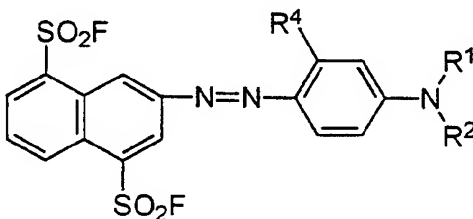
The procedure of Example 139 was used except that 1-(N-ethyl-N-n-propylamino) naphthalene was used in place of the 3-(N,N-diethylamino) acetanilide. The dye has a  $\lambda_{\max}$  of 578nm.

Example 252Preparation of 4-(4,8-difluorosulphonylnaphth-2-ylazo)-N,N-diethylaniline

To a mixture of 2-amino-4,8difluorosulphonylnaphthalene (1.6 parts) and acetic/propionic acid mixture (20 parts, 86/14 vol/vol), stirring at 0.5°C, was added dropwise nitrosyl sulphuric acid soln (1.5 parts). The mixture was stirred at this temperature for a further 15 mins.

The diazo solution was added to a mixture of N,N-diethylaniline (0.9 parts), methanol (50 parts) and sulphamic acid (0.5 parts); stirring at 0.5°C. After stirring for 2 hours at this temperature, the product was isolated by filtration, washed with water and dried at 50°C to yield; 4-(4,8-difluorosulphonylnaphthyl-2-azo)-N,N-diethylaniline (1.6 parts). When applied to polyester materials from an aqueous dispersion, the dye gives red shades with excellent fastness to wet treatments.  $\lambda_{\max}$  of 500nm.

The following Examples of dyes of Formula:



were prepared by the procedure of Example 252:

Example	R <sup>1</sup>	R <sup>2</sup>	R <sup>4</sup>	$\lambda_{\text{max}}$
253	-C <sub>4</sub> H <sub>9</sub>	-C <sub>4</sub> H <sub>9</sub>	-H	509
254	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	519
255	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-NHCOCH <sub>3</sub>	530
256	-C <sub>2</sub> H <sub>4</sub> CN	-C <sub>2</sub> H <sub>4</sub> CN	-H	460

#### Example 257

##### Preparation of 4-(2-cyano-4-nitrophenylazo)-N-ethyl-N-2-(4-fluorosulphonylphenoxy)ethylaniline

To a mixture of 2-cyano-4-nitroaniline (1.5 parts) and acetic/propionic acid mixture (10 parts, 86/14 vol/vol), stirring at 0.5°C, was added dropwise nitrosyl sulphuric acid soln (2.0 parts). The mixture was stirred at this temperature for a further 30 mins.

The diazo solution was added to a mixture of N-ethyl,N-2-(4-fluorosulphonylphenoxy)-ethylaniline (3.0 parts), methanol (50 parts) and sulphamic acid (0.5 parts); stirring at 0.5°C. After stirring for 2 hours at this temperature, the product was isolated by filtration, washed with water and dried at 50°C to yield; 4-(2-cyano-4-nitrophenylazo)-N-ethyl,N-2-(4-fluorosulphonylphenoxy)ethylaniline (3.0 parts). When applied to polyester materials from an aqueous dispersion, the dye gives bluish red shades with excellent light fastness and excellent fastness to wet treatments.  $\lambda_{\text{max}}$  of 530nm.

#### Example 258

##### Preparation of 4-(3-acetyl-5-nitrothien-2-ylazo)-N-ethyl-N-2-(4-fluorosulphonylphenoxy) ethylaniline

The procedure of Example 257 was repeated except that in place of the 1.5 parts of 2-cyano-4-nitroaniline; 1.7 parts of 2-amino-3-acetyl-5-nitrothiophene were used. The product 4-(3-acetyl-5-nitrothienyl-2-azo)-N-ethyl,N-2-(4-fluorosulphonylphenoxy)ethylaniline (2.0 parts) when applied to polyester materials from an aqueous dispersion gives reddish blue shades with excellent fastness to light and wet treatments.  $\lambda_{\text{max}}$  of 590nm.

#### Example 259

##### Preparation of 4-(2-chloro-4-nitrophenylazo)-3-methyl-N-ethyl-N-2-(4-fluorosulphonylphenoxy)ethylaniline

To chlorosulphonic acid (17.5 parts) stirring at 0.5°C, was added gradually 3-methyl-4-(2-chloro-4-nitrophenylazo)-N-ethyl,N-2-phenoxyethylaniline (8.0 parts). Thionyl chloride (5.4 parts) was added and the mixture was stirred at 0.5°C for 2 hours. The reaction mixture was drowned into ice/water (500 parts), the product was isolated



by filtration and washed acid-free with cold water.

The filter cake was set stirring with 1,4-dioxan (40 parts) and a solution of potassium fluoride (1.8 parts) in water (10 parts) was added. The mixture was heated at 60°C for 3 hours, cooled to ambient and the product was isolated by filtration to yield; 3-methyl-4-(2-chloro-4-nitrophenylazo)-N-ethyl,N-2-(4-fluorosulphonylphenoxy)ethylaniline (4.5 parts).

The product when applied to polyester materials from an aqueous dispersion gives mid red shades with excellent fastness to light and wet treatments.  $\lambda_{\max}$  of 510nm.

Example 260

Preparation of 4-(6-thiocyanatobenzothiazol-2-ylazo)-N-ethyl-N-2-(4-fluorosulphonylphenoxy)ethylaniline

The procedure of Example 257 was repeated except that in place of the 1.5 parts of 2-cyano-4-nitroaniline; 1.9 parts of 2-amino-6-thiocyanatobenzthiazole were used.

The product, 4-(6-thiocyanatobenzthiazolyl-2-azo)-N-ethyl,N-2-(4-fluorosulphonylphenoxy)ethylaniline (1.4 parts) when applied to polyester materials from an aqueous dispersion gives bluish red shades with excellent fastness to light and wet treatments.  $\lambda_{\max}$  of 522nm.

Example 261

Preparation of 4-(2,6-dichloro-4-nitrophenylazo)-N-ethyl-N-2-(4-fluorosulphonylphenoxy)ethylaniline

The procedure of Example 257 was repeated except that in place of the 1.5 parts of 2-cyano-4-nitroaniline; 1.9 parts of 2-amino-6-thiocyanatobenzthiazole were used.

The product, 4-(6-thiocyanatobenzthiazolyl-2-azo)-N-ethyl,N-2-(4-fluorosulphonylphenoxy)ethylaniline (1.4 parts) when applied to polyester materials from an aqueous dispersion gives bluish red shade with excellent fastness to light and wet treatments.  $\lambda_{\max}$  of 522nm.

Example 262

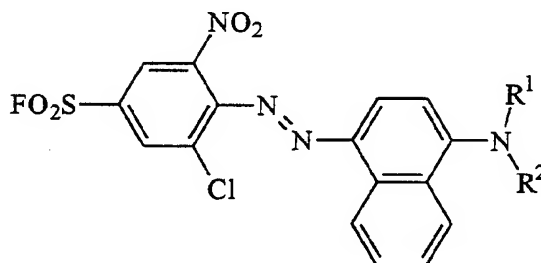
Preparation of 4-(6-thiocyanatobenzothiazol-2-ylazo)-3-methyl-N-ethyl-N-2-(4-fluorosulphonylphenoxy)ethylaniline

The procedure of Example 257 was repeated except that in place of the 3.0 parts of N-ethyl,N-2-(4-fluorosulphonylphenoxy)ethylaniline, 3.1 parts of N-ethyl,N-2-(4-fluorosulphonylphenoxy)ethyl-m-toluidine were used.

The product, 3-methyl-4-(6-thiocyanatobenzthiazolyl-2-azo)-N-ethyl,N-2-(4-fluorosulphonylphenoxy)ethylaniline (1.7 parts) when applied to polyester materials from an aqueous dispersion gives violet shades with excellent fastness to light and wet treatments.  $\lambda_{\max}$  of 540nm.

Examples 263 and 264

Dyes prepared by the procedure described for Example 139 but using the 1-naphthylamine in place of 3-(N,N-diethylamino)acetanilide are of Formula :



Example	R <sub>1</sub>	R <sub>2</sub>	$\lambda_{\text{max}}$ /nm
263	C <sub>2</sub> H <sub>5</sub>	H	571
264	C <sub>2</sub> H <sub>5</sub>	C <sub>3</sub> H <sub>7</sub>	578

Example 265Preparation of 1-n-butyl-5-(2,5-dichloro-4-fluorosulphonylphenylazo)-3-cyano-6-hydroxy-4-methyl-2-oxo-1H-pyridine

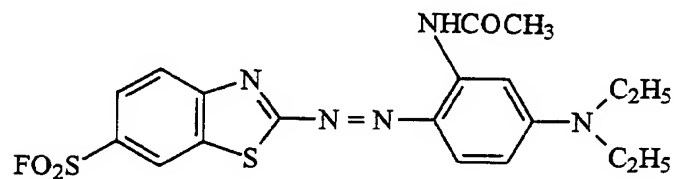
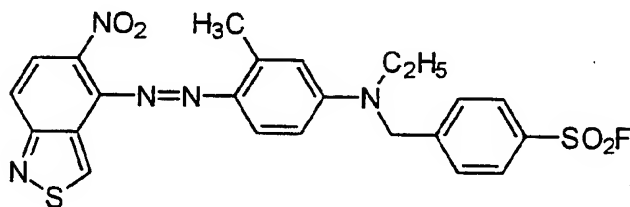
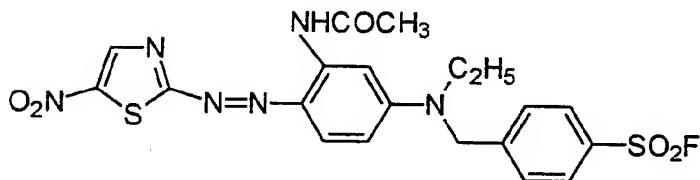
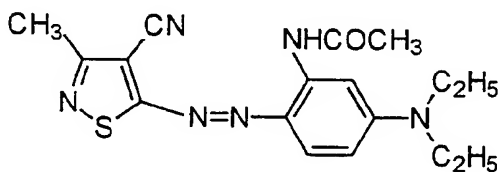
The procedure of Example 1 was repeated except that in place of the 3.0g of 3-methyl-N-ethyl-N-(2-benzoyloxyethyl)aniline, 1.8g of 1-n-butyl-3-cyano-6-hydroxy-4-methyl-2-oxo-1H-pyridine were used. The product 1-n-butyl-5-(2,5-dichloro-4-fluorosulphonylphenylazo)-3-cyano-6-hydroxy-4-methyl-2-oxo-1H-pyridine (2.5g) when applied to polyester materials from aqueous dispersion gives greenish yellow shades with excellent wet and light fastness properties.  $\lambda_{\text{max}}$ =435nm.

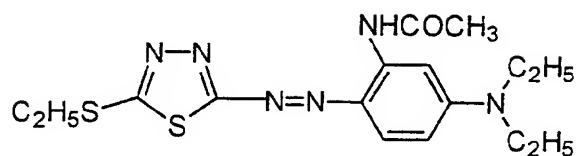
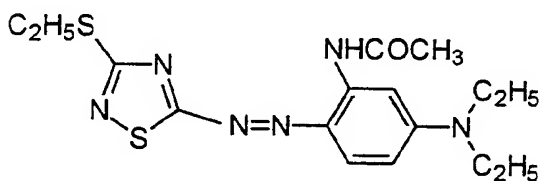
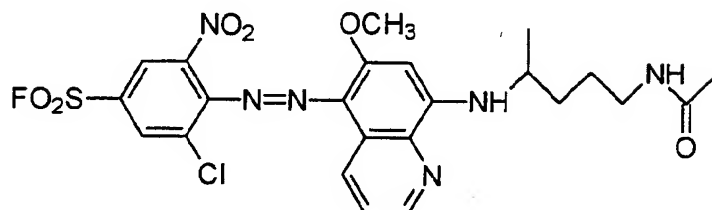
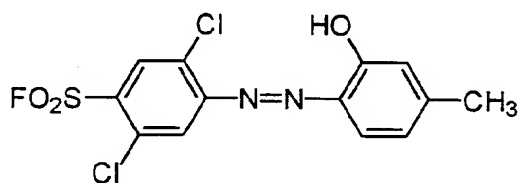
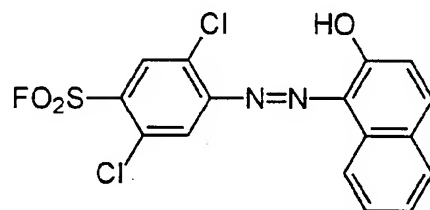
Example 266Preparation of 1-phenyl-3-t-butyl-5-amino-4-(2,5-dichloro-4-fluorosulphonylphenylazo) pyrazole

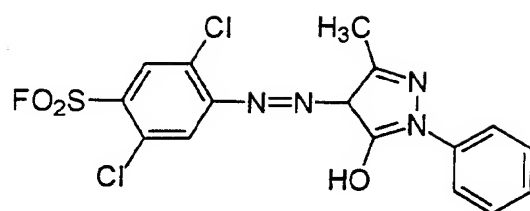
The procedure of Example 1 was repeated except that in place of the 3.0g of 3-methyl-N-ethyl-N-(2-benzoyloxyethyl)aniline, 1.5g of 1-phenyl-3-t-butyl-5-aminopyrazole were used. The product 1-phenyl-3-t-butyl-5-amino-4-(2,5-dichloro-4-fluorosulphonylphenylazo) pyrazole (2.1g) when applied to polyester materials from aqueous dispersion gives greenish yellow shades with excellent wet and light fastness properties.  $\lambda_{\text{max}}$ =442nm.

Examples 267-278

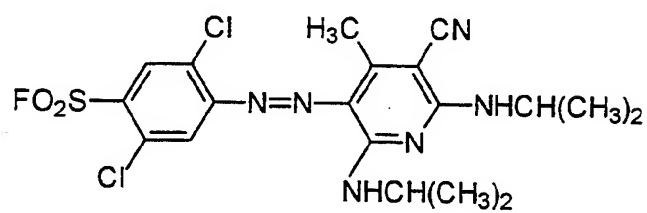
The dyes of the following formulae may be made by the procedure of Example 1 by diazotising the appropriate amine and coupling onto the appropriate coupling component :-

Example 267Example 268Example 269Example 270

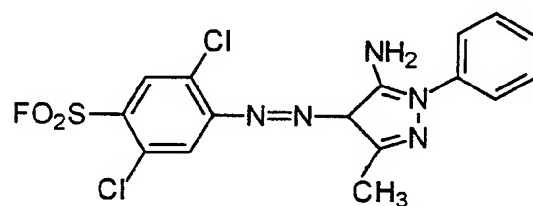
Example 271Example 272Example 273Example 274Example 275

Example 276

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Example 277

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Example 278

CLAIMS

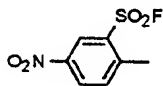
1. A process for colouring a synthetic textile material or fibre blend thereof which comprises applying to the synthetic textile material a compound or mixture thereof, which is free from water solubilising groups, of Formula (1):



Formula (1)

wherein:

A and D each independently is an optionally substituted heterocyclic or carbocyclic group and at least one of A or D carries directly at least one  $-SO_2F$  group or carries a substituent to which at least one  $-SO_2F$  group is attached except for 4-(4-fluorosulphonylphenylazo)-N,N-dimethylaniline, provided that one of A or D is not 3,5-difluorosulphonylthien-2-yl, optionally substituted 1-phenyl-pyrazol-4-yl-5-one or



or that one of A or D does not carry an  $-NCH_2CH(OH)CH_2Cl$ ,  $-NCOCH_2Cl$  or  $-NCH_2CH_2SO_2F$  substituent.

2. A process for colouring a synthetic textile material or fibre blend thereof which comprises applying to the synthetic textile material a compound or mixture thereof, which is free from water solubilising groups, of Formula (1) wherein A and D each independently is an optionally substituted heterocyclic or carbocyclic group in which at least one of A or D carries directly at least one  $-SO_2F$  group or carries a substituent to which at least one  $-SO_2F$  group is attached and at least one of A or D carries directly at least one ester group or carries a substituent to which at least one ester group is attached.

3. A process for colouring a polyester textile material or fibre blend thereof which comprises applying to the polyester textile material a compound or mixture thereof, which is free from water solubilising groups, of Formula (1) in which A and D are as herein before defined except for 4-(4-fluorosulphonylphenylazo)-N,N-dimethylaniline, provided that one of A or D is not 3,5-

difluorosulphonylthien-2-yl, optionally substituted 1-phenylpyrazol-4-yl-5-one or 4-nitro-2-fluorosulphonylphenyl or that one of A or D does not carry an  $-NCH_2CH_2SO_2F$  substituent.

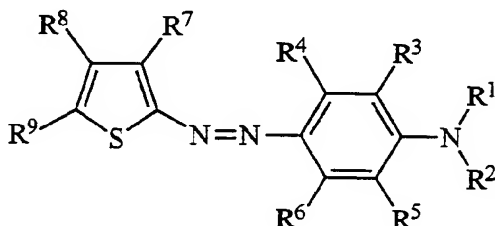
4. A process according to any one of claims 1 to 3 in which A and D each independently is selected from thienyl, thiazolyl, isothiazolyl, pyrazolyl, imidazolyl, pyridyl, pyridonyl, 1,2,4- and 1,3,4-thiadiazolyl, furanyl, pyrrolyl, pyridazyl, pyrimidyl, pyrazinyl, benzothiazolyl, benzoisothiazolyl, quinolinyl, isoquinolinyl, indolyl, pyridothiazolyl, pyridoisothiazolyl, 1,2,3-triazolyl, 1,2,4-triazolyl, phenyl and naphthyl.

5. A process according to any one of claims 1 to 3 in which A and D each independently is selected from thienyl, phenyl, naphthyl, thiazolyl, isothiazolyl, pyridonyl, quinolinyl.

6. A process according to any one of claims 1 to 3 in which A and D each independently is selected from thien-2-yl, phenyl, naphth-1-yl, naphth-2-yl, thiazol-2-yl, isothiazol-5-yl, pyrid-4-one-5-yl or quinolinyl.

7. A process according to any one of claims 1 to 3 in which A is thien-2-yl or phenyl and D is phenyl or naphth-1-yl.

8. A process according to any one of claims 1 to 3 in which the compound of Formula (1) is of Formula (3):



Formula (3)

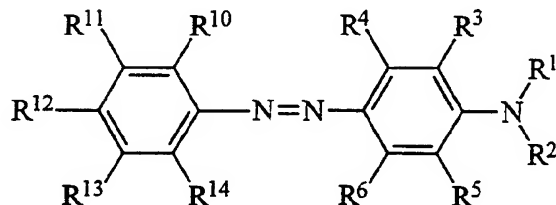
wherein:

R<sup>1</sup> and R<sup>2</sup> each independently is -H or optionally substituted C<sub>1-6</sub>-alkyl or optionally substituted aryl;

R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each independently is -H, -F, -Cl, -Br, -I, -SO<sub>2</sub>F or C<sub>1-6</sub>-alkyl, C<sub>1-6</sub>-alkoxy, C<sub>1-4</sub>alkanoylamino, -NHSO<sub>2</sub>alkyl or

-Ophenyl each of which may be optionally substituted;  
 R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup> each independently is -H, C<sub>1-6</sub>-alkyl, -NO<sub>2</sub>, -COOC<sub>1-6</sub>-alkyl,  
 -OCOalkyl, -Cl, -F, -Br, -I, -COC<sub>1-6</sub>-alkyl, -CN, formyl,  
 protected formyl or -SO<sub>2</sub>F provided that at least one of R<sup>1</sup> to  
 R<sup>9</sup> is -SO<sub>2</sub>F or carries a substituent to which at least one  
 -SO<sub>2</sub>F group is attached and provided that R<sup>7</sup> and R<sup>9</sup> are not  
 both -SO<sub>2</sub>F.

9. A process according to any one of claims 1 to 3 in which the  
 compound of Formula (1) is of Formula (4):



Formula (4)

wherein:

R<sup>1</sup> and R<sup>2</sup> each independently is -H or optionally substituted C<sub>1-6</sub>-alkyl or  
 optionally substituted aryl;

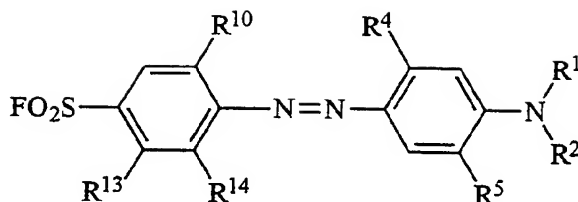
R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each independently is -H, -F, -Cl, -Br, -I, -SO<sub>2</sub>F or  
 C<sub>1-6</sub>alkyl, C<sub>1-6</sub>-alkoxy, C<sub>1-4</sub>-alkanoylamino, -NHSO<sub>2</sub>alkyl or -  
 Ophenyl each of which may be optionally substituted; and

R<sup>10</sup> to R<sup>14</sup> each independently is -H, alkoxy, alkyl, -NO<sub>2</sub>, -SO<sub>2</sub>F, -F, -Cl,  
 -Br, -I or -CN;

provided that when R<sup>10</sup> is SO<sub>2</sub>F, R<sup>12</sup> is not -NO<sub>2</sub> and R<sup>11</sup>, R<sup>13</sup> and R<sup>14</sup> are not  
 all -H.

10. A process according to any one of claims 1 to 3 in which the  
 compound of Formula (1) is of Formula (7):



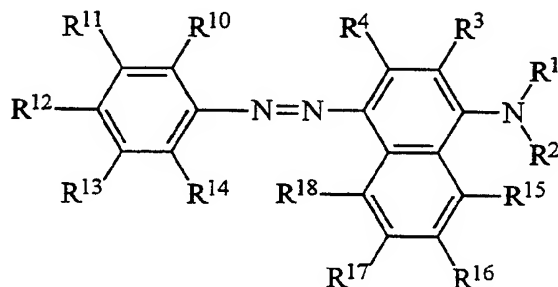


Formula (7)

in which

- R<sup>1</sup> and R<sup>2</sup> each independently is optionally substituted C<sub>1-6</sub>-alkyl;  
 R<sup>4</sup> is alkyl or a group of Formula R<sup>19</sup>-N-Y-X-W  
 in which Y is a direct link or C = O, X is a direct link, alkyl, alkenyl, aryl, heterocyclic, alkylOalkyl, -NR<sup>20</sup>-Z-, -COOZ or -O-Z in which Z is alkyl, alkenyl, aryl, heterocyclic, alkylOalkyl or a direct link and  
 R<sup>20</sup> is -H, alkyl, aryl or alkylaryl, W is -CO<sub>2</sub>R<sup>21</sup>, -OCOR<sup>21</sup> or -OH in which R<sup>21</sup> is alkyl, aryl, alkylaryl, alkylOalkyl or alkylOH, and R<sup>19</sup> is -H or alkyl;  
 R<sup>5</sup> is -H, C<sub>1-6</sub>-alkoxy or -Ophenyl;  
 R<sup>10</sup> is -NO<sub>2</sub> or -Cl; and  
 R<sup>13</sup> and R<sup>14</sup> each independently is -H or -Cl.

11. A process according to any one of claims 1 to 3 in which the compound of Formula (1) is of Formula (5):



Formula (5)

wherein

R<sup>1</sup> and R<sup>2</sup> each independently is -H, optionally substituted C<sub>1-6</sub>-alkyl;

R<sup>3</sup> is optionally substituted C<sub>1-6</sub>-alkyl or C<sub>1-6</sub>-alkoxy;

R<sup>4</sup> is optionally substituted C<sub>1-6</sub>-alkyl or C<sub>1-6</sub>-alkoxy;

5 R<sup>10</sup> is optionally substituted C<sub>1-6</sub>-alkyl, NO<sub>2</sub> or Cl;

R<sup>15</sup> to R<sup>18</sup> each independently is -H, -C<sub>1-6</sub>-alkyl, -C<sub>1-6</sub>-alkoxy, -F, -Cl, -Br, -I, -SO<sub>2</sub>F, -NO<sub>2</sub>, -CN or -NR<sup>1</sup>R<sup>2</sup>;

R<sup>12</sup> is -NO<sub>2</sub> or -SO<sub>2</sub>F;

R<sup>11</sup> is -H; and

10 R<sup>13</sup> and R<sup>14</sup> each independently is -H or -Cl.

12. A compound of Formula (2):



15 Formula (2)

in which:

A<sup>1</sup> and D<sup>1</sup> each independently is an optionally substituted heterocyclic or carbocyclic group

and at least one of A<sup>1</sup> or D<sup>1</sup> carries directly at least one -SO<sub>2</sub>F group or carries a substituent to which at least one -SO<sub>2</sub>F group is attached

20 except for 4-(4-fluorosulphonylphenylazo)-N,N-dimethylaniline,

4-(4-fluorosulphonylphenylazo)-N,N-diethylaniline,

4-(4-fluorosulphonylphenylazo)-N-ethyl-N-acetoxyethylaniline,

1-(5-fluorosulphonyl-2-methylphenylazo)-2-hydroxynaphthalene,

25 4-(4-fluorosulphonylphenylazo)-3-(trifluoromethylcarbonylamino)-N-ethyl-N-(2-methoxyethyl)aniline,

4-(4-fluorosulphonylphenylazo)-3-(trifluoromethylcarbonylamino)-N-ethyl-N-(2-cyanoethyl)aniline,

4-(4-fluorosulphonylphenylazo)-2,5-dimethyl-N-ethyl-N-(2-methoxyethyl)aniline,

30 4-(4-fluorosulphonylphenylazo)-2,5-dimethyl-N-ethyl-N-(2-cyanoethyl)aniline,

4-(4-fluorosulphonylphenylazo)-N-ethyl-N-(2-fluorosulphonylethyl)aniline,

35 4-(4-fluorosulphonylphenylazo)-N,N-di(2-fluorosulphonylethyl)aniline,

4-(3-fluorosulphonyl-4-methylphenylazo)-3-(trifluoromethylcarbonylamino)-N-ethyl-N-(2-methoxyethyl)aniline,

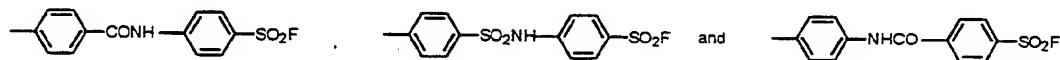
4-(3-fluorosulphonyl-4-methylphenylazo)-2,5-dimethyl-N-ethyl-N-(2-methoxyethyl)aniline,

40 4-(3-fluorosulphonyl-4-chlorophenylazo)-3-(trifluoromethylcarbonylamino)-N-ethyl-N-(2-methoxyethyl)aniline,

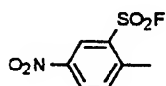
4-(3-fluorosulphonyl-4-chlorophenylazo)-2,5-dimethyl-N-ethyl-N-(2-methoxyethyl)aniline,

4-(5-fluorosulphonyl-2-methylphenylazo)-1-aminonaphthalene,

4-(5-fluorosulphonyl-2-methylphenylazo)-2-ethoxyaniline,  
 4-(3-fluorosulphonylphenylazo)-2,5-dimethoxyaniline,  
 4-(2-chloro-4-nitrophenylazo)-2-methyl-5-fluorosulphonylaniline,  
 provided that A<sup>1</sup> is not 3,5-difluorosulphonylthien-2-yl, optionally  
 substituted pyrazol-4-yl-5-one or N-allylpyrid-2-one-5-yl and provided  
 that A<sup>1</sup> is not

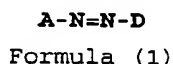


when D<sup>1</sup> carries an -NCH<sub>2</sub>CH(OH)CH<sub>2</sub>Cl substituent and provided that one of  
 A<sup>1</sup> or D<sup>1</sup> is not



and provided that A<sup>1</sup> is not a fluorosulphonylphenyl group when D<sup>1</sup> is an  
 arylamide of an aromatic 2-hydroxycarboxylic acid.

13. A compound of Formula (1):



wherein

A and D each independently is an optionally substituted heterocyclic or  
 carbocyclic group in which at least one of A or D carries directly at  
 least one -SO<sub>2</sub>F group or carries a substituent to which at least one -  
 SO<sub>2</sub>F group is attached and at least one of A or D carries directly at  
 least one ester group or carries a substituent to which at least one  
 ester group is attached.

14. A compound according to claim 13 in which A and D each  
 independently is selected from thienyl, thiazolyl, isothiazolyl,  
 pyrazolyl, imidazolyl, pyridyl, pyridonyl, 1,2,4- and 1,3,4-  
 thiadiazolyl, furanyl, pyrrolyl, pyridazyl, pyrimidyl, pyrazinyl,  
 benzothiazolyl, benzoisothiazolyl, quinolinyl, isoquinolinyl, indolyl,  
 pyridothiazolyl, pyridoisothiazolyl, 1,2,3-triazolyl, 1,2,4-triazolyl,  
 phenyl and naphthyl.

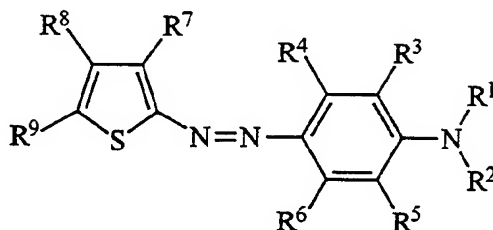
15. A compound according to claim 13 in which A and D each  
 independently is selected from thienyl, phenyl, naphthyl, thiazolyl,

isothiazolyl, pyridonyl, quinolinyl.

16. A compound according to claim 13 in which A and D each independently is selected from thien-2-yl, phenyl, naphth-1-yl, naphth-2-yl, thiazol-2-yl, isothiazol-5-yl, pyrid-4-one-5-yl or quinolinyl.

17. A compound according to claim 13 in which A is thien-2-yl or phenyl and D is phenyl or naphth-1-yl.

18. A compound according to claim 13 in which the compound of Formula (1) is of Formula (3):



Formula (3)

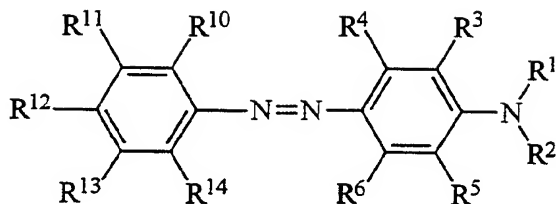
wherein:

R<sup>1</sup> and R<sup>2</sup> each independently is -H or optionally substituted C<sub>1-6</sub>-alkyl or optionally substituted aryl;

R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each independently is -H, -F, -Cl, -Br, -I, -SO<sub>2</sub>F or C<sub>1-6</sub>-alkyl, C<sub>1-6</sub>-alkoxy, C<sub>1-4</sub>alkanoylamino, -NHSO<sub>2</sub>alkyl or -Ophenyl each of which may be optionally substituted;

R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup> each independently is -H, C<sub>1-6</sub>-alkyl, -NO<sub>2</sub>, -COOC<sub>1-6</sub>-alkyl, -OCOalkyl, -Cl, -F, -Br, -I, -COC<sub>1-6</sub>-alkyl, -CN, formyl, protected formyl or -SO<sub>2</sub>F provided that at least one of R<sup>1</sup> to R<sup>9</sup> is -SO<sub>2</sub>F or carries a substituent to which at least one -SO<sub>2</sub>F group is attached and provided that R<sup>7</sup> and R<sup>9</sup> are not both -SO<sub>2</sub>F.

19. A compound according to claim 13 in which the compound of Formula (1) is of Formula (4):



Formula (4)

wherein:

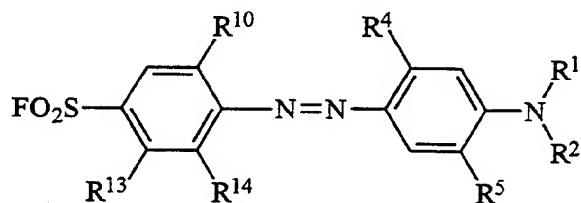
R<sup>1</sup> and R<sup>2</sup> each independently is -H or optionally substituted C<sub>1-6</sub>-alkyl or optionally substituted aryl;

R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each independently is -H, -F, -Cl, -Br, -I, -SO<sub>2</sub>F or C<sub>1-6</sub>-alkyl, C<sub>1-6</sub>-alkoxy, C<sub>1-4</sub>-alkanoylamino, -NHSO<sub>2</sub>alkyl or -Ophenyl each of which may be optionally substituted; and

R<sup>10</sup> to R<sup>14</sup> each independently is -H, alkoxy, alkyl, -NO<sub>2</sub>, -SO<sub>2</sub>F, -F, -Cl, -Br, -I or -CN;

provided that when R<sup>10</sup> is SO<sub>2</sub>F, R<sup>12</sup> is not -NO<sub>2</sub> and R<sup>11</sup>, R<sup>13</sup> and R<sup>14</sup> are not all -H.

20. A compound according to claim 13 in which the compound of Formula (1) is of Formula (7):



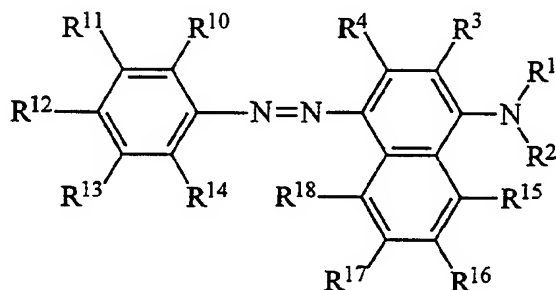
Formula (7)

in which

R<sup>1</sup> and R<sup>2</sup> each independently is optionally substituted C<sub>1-6</sub>-alkyl;  
 R<sup>4</sup> is alkyl or a group of Formula R<sup>19</sup>-N-Y-X-W  
 in which Y is a direct link or C = O, X is a direct link, alkyl, alkenyl, aryl, heterocyclic, alkylalkyl, -NR<sup>20</sup>-Z-, -

COOZ or -O-Z in which Z is alkyl, alkenyl, aryl, heterocyclic, alkylalkyl or a direct link and  
 $R^{20}$  is -H, alkyl, aryl or alkylaryl, W is  $-\text{CO}_2R^{21}$ ,  $-\text{OCOR}^{21}$  or -OH  
 in which  $R^{21}$  is alkyl, aryl, alkylaryl, alkylalkyl or  
 alkylOH, and  $R^{19}$  is -H or alkyl;  
 $R^5$  is -H,  $\text{C}_{1-6}$ -alkoxy or -Ophenyl;  
 $R^{10}$  is  $-\text{NO}_2$  or -Cl; and  
 $R^{13}$  and  $R^{14}$  each independently is -H or -Cl.

21. A compound according to claim 13 in which the compound of Formula (1) is of Formula (5):

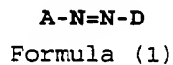


Formula (5)

wherein

$R^1$  and  $R^2$  each independently is -H, optionally substituted  $\text{C}_{1-6}$ -alkyl;  
 $R^3$  is optionally substituted  $\text{C}_{1-6}$ -alkyl or  $\text{C}_{1-6}$ -alkoxy;  
 $R^4$  is optionally substituted  $\text{C}_{1-6}$ -alkyl or  $\text{C}_{1-6}$ -alkoxy;  
 $R^{10}$  is optionally substituted  $\text{C}_{1-6}$ -alkyl,  $\text{NO}_2$  or Cl;  
 $R^{15}$  to  $R^{18}$  each independently is -H,  $-\text{C}_{1-6}$ -alkyl,  $-\text{C}_{1-6}$ -alkoxy, -F, -Cl, -Br, -I,  $-\text{SO}_2\text{F}$ ,  $-\text{NO}_2$ , -CN or  $-\text{NR}^1\text{R}^2$ ;  
 $R^{12}$  is  $-\text{NO}_2$  or  $-\text{SO}_2\text{F}$ ;  
 $R^{11}$  is -H; and  
 $R^{13}$  and  $R^{14}$  each independently is -H or -Cl.

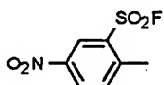
22. A dispersion comprising a compound of Formula (1):



wherein

A and D each independently is an optionally substituted heterocyclic or

carbocyclic group and  
at least one of A or D carries directly at least one  $-\text{SO}_2\text{F}$  group or  
carries a substituent to which at least one  $-\text{SO}_2\text{F}$  group is attached  
except for 4-(4-fluorosulphonylphenylazo)-N,N-dimethylaniline, provided  
5 that one of A or D is not 3,5-difluorosulphonylthien-2-yl, optionally  
substituted 1-phenyl-pyrazol-4-yl-5-one or



or that one of A or D does not carry an  $-\text{NCH}_2\text{CH}(\text{OH})\text{CH}_2\text{Cl}$ ,  $-\text{NCOCH}_2\text{Cl}$  or  
 $-\text{NCH}_2\text{CH}_2\text{SO}_2\text{F}$  substituent and water.

15 23. A process for the mass coloration of plastics which  
comprises incorporating into a plastics material a compound or mixture  
thereof which is free from water solubilising groups, of Formula (1)  
wherein A and D each independently is an optionally substituted  
20 heterocyclic or carbocyclic group and at least one of A or D carries  
directly at least one  $-\text{SO}_2\text{F}$  group or carries a substituent to which at  
least one  $-\text{SO}_2\text{F}$  group is attached.

25 24. A process for the mass coloration of plastics which  
comprises incorporating into a plastics material a compound or mixture  
thereof which is free from water solubilising groups, of Formula (1)  
wherein A and D each independently is an optionally substituted  
heterocyclic or carbocyclic group and at least one of A or D carries  
20 directly at least one  $-\text{SO}_2\text{F}$  group or carries a substituent to which at  
least one  $-\text{SO}_2\text{F}$  group is attached and at least one of A or D carries  
30 directly at least one ester group or carries a substituent to which at  
least one ester group is attached.

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 94/02831

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09B62/825 C09B29/01 C09B29/033 C09B29/08 C09B29/36  
C09B29/10 C09B29/095 D06P3/26 D06P3/82 C08K5/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09B D06P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,856 348 (WESTMINSTER BANK LTD.) 14 December 1960  see claims; example 24 ---	1-7, 12-17, 22-24
X	GB,A,819 664 (SANDOZ LTD.) 9 September 1959  see claims; example 2 ---	1-7, 12-17,22
X	US,A,3 131 021 (W BAIRD ET AL.) 28 April 1964  see claims 1-7, examples 2,6 see examples 28-52,54-56 ---	1,12
X	US,A,2 576 037 (R.P.PARKER ET AL.) 20 November 1951  see the whole document ---	1,12,22
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 94/02831

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X	FR,A,1 192 485 (CIBA) 27 October 1959 see page 4, example 1 and table, compounds 1,3,4 ---	1,12
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X	GB,A,2 108 993 (KODAK LTD) 25 May 1983  see page 3, lines 4,5,13,20,23,24, page 4, lines 41,42, page 5, lines 10,12,26,27,34 see page 6, line 6 - line 9 -----	1-7, 12-17,22

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Information on patent family members

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